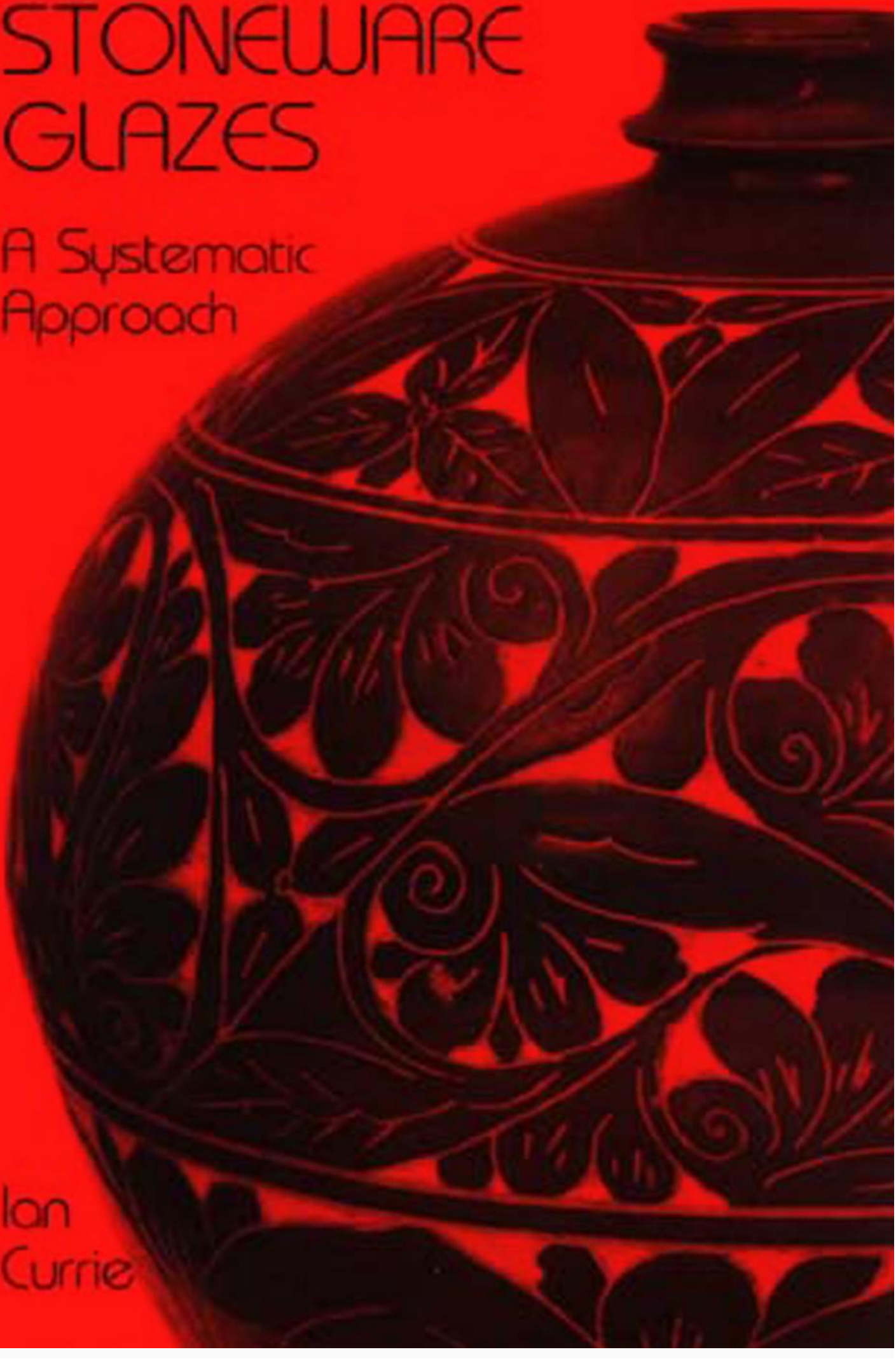
STONEWARE GLAZES

A Systematic Approach



Ian Currie

STONEWARE GLAZES

A Systematic Approach

Second Edition

Ian Currie

Bootstrap Press

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For my parents,
Sam and Marie Currie,
with love.

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Numerous other acknowledgements are made within the text of the book.

I would like finally to acknowledge the loving support provided by Christine, Hamish and Nell.

I.S.C.

CONTENTS

FOREWORD

EXPLANATORY OUTLINE

Practical Guide. Base glazes — a key to understanding glaze principles. Limits. Methodology.

PART I — BASE GLAZES

1 PREPARATIONS 2

Introduction. Group study. Reference books. Base glaze theory and practice. Raw materials. Guidelines for selection of materials.

2 BASIC CHEMISTRY 10

Atoms. Molecules. Oxides. Glaze — a glassy mix of oxides. The relationship between recipe, oxide weight % and Seger formula. Converting a Seger formula to oxide weight %. Converting a Seger formula to a recipe.

3 GETTING STARTED — MATERIAL REQUIREMENTS 16

Glaze materials. Clay materials. Equipment and books.

4 LINE BLENDS — ASH, CLAY AND ROCK GLAZES 20

Wood ash. Clay. Rock dust. Ball Mills. Volumetric blending — a lot of glazes with a little work. References.

5 BASELINE GRIDS AND BIAXIAL BLENDS 25

Baseline grids. Biaxial blends.

6 EXPERIMENTAL PROCEDURE FOR BIAXIAL BLENDS 28

Making the glazes. Applying the glazes and oxides and firing. Assessment tiles and individual tiles. Putting the results in order. Assessment of results.

7 ALUMINA AND SILICA IN STONEWARE GLAZES 36

Effects of varying alumina and silica. Sources of alumina in glazes. Sources of silica in glazes. The alumina/silica ratio.

8 LIME ALKALI GLAZES 43

The use of calcium in stoneware glazes. Sources of calcium. The use of alkali fluxes in stoneware glazes. Sources of alkalis. Preliminary comments on experiments. The 0.9 Limestone Set. The 0.8 Limestone Set. The 0.7 Limestone Set. The 0.6 Limestone Set. The 0.6 Feldspar Set.

9 MAGNESIUM GLAZES 62

Sources of magnesia. The Magnesium Set. Alternative recipes for the Magnesium Set. Intermediate sets.

10 ZINC GLAZES 68

Sources of zinc. The Zinc Set. Intermediate sets.

11 BARIUM GLAZES 74

Sources of barium. Barium carbonate is poisonous. Intermediate sets. The Barium Set. The Barium Alkaline Set.

12 DESIGNING AN EXPERIMENT 82

Design your own base glaze experiment.

13 PHASE EQUILIBRIA DIAGRAMS AND EUTECTICS 84

Simple phase equilibria diagrams. More complicated P.E. diagrams. Triaxial diagrams. The effect of increasing the number of ingredients. Reading triaxial phase diagrams. Summary. References.

14 CALCULATIONS 92

Converting formula to recipe. The Four Question technique. Percentage calculation. Formula to recipe — model conversion. Exercises. List of raw materials. Conversion of a glaze recipe to a Seger formula. Conversion of analysis data (%) to Seger formula and molecular weight. Formula to recipe — a more difficult example. Simultaneous Equations. The percentage method of glaze calculation. More formula to recipe. Calcining calculations. Parts chart calculations. Partial blends and intermediate blends. Calculating blended glaze recipes.

PART II — SPECIFIC GLAZES

15 METHODOLOGY 120

Outline. A reference framework for molecular formulae. Test firings. Draw trials. Oxidation — neutral — reduction atmospheres. Mortar and pestle line blending technique.

16 CRYSTALLINE GLAZES 124

Devitrification — glass giving rise to crystals. The process of crystallisation. Important factors in crystal growth. Different types of crystalline glazes. Exercises. References.

17 MATT GLAZES 134

Introduction. The clay — glaze interface. Exercises: Flux Matts. Alumina matts. Silica matts. References.

18 OPAQUE GLAZES. CHUN-BLUE GLAZES 141

Introduction. Opaque glazes. Chun-blue glazes. The chun-blue effect. Factors affecting the development of chun-blue. Chun-type glaze recipes. References.

19 DECORATED WHITEWARE. GLAZE FIT 150

Introduction. Whiteness — how will you get it? Body. White slip. Colours. Glazes. Glaze fit. References.

20 HIGH IRON GLAZES 158

Introduction. Forms of iron oxide in glazes. Unity formula convention for iron glazes. Experiments. Discussion of results including iron solubility, rust break, chun-blue occurrence and teadust crystals. Specific iron glazes, including honey, tenmoku, kaki, oilspot tenmoku, teadust, tomato red and tessha glazes, and iron glazes using natural materials. References. "High Iron Stoneware Glazes" by R. R. Hughan.

21 CELADON 173

Introduction. The base glaze — its role in celadon glazes. Lung Chuan celadon. Blue celadon. Bubbles in celadon. References.

22 KUAN GLAZES 179

Description and the problems involved. Suggested research program. References.

23 SHINO GLAZES 183

Traditional Japanese Shino. Nepheline syenite Shino. 'Fire colour' in Shino. Technical notes. References.

24 COPPER GLAZES 188

Copper as a colourant. Oxidised copper glazes. Reduced copper glazes — copper reds. References.

25 NATURAL GLAZES FROM WOODFIRING 194

Introduction. Typical Shigaraki climbing kiln. Using a smaller kiln. A Bizen Kiln. A few hints. Extended firings — glazed and unglazed pots. Ash types and clay types. References.

26 ROCK GLAZES 200

Igneous rocks. Identifying rocks and minerals. Crushing and grinding the rock. Ivan Englund on rock glazes. Some simple testing procedures. References. Extract: 'Borax Bead Test'.

INDEX 209

FOREWORD

This course on stoneware glazes began with an investigation of the Japanese approach to the subject in 1972 during a year's study of ceramics in Japan. In a series of tutorials Masataro Onishi, then the head of the Kyoto Ceramic Research Centre, outlined to me the way he taught glaze technology, basically using a careful consideration of glaze materials, clay body and firing, using the Seger formula and an alumina/silica chart as a starting point to explain glaze phenomena by a consideration of the base glaze. I also obtained a copy of a Japanese text, *Fundamentals of Glaze Technology* by Etsuzo Kado, that was widely used to teach the subject, and much of this was translated for me by my Japanese sponsor, Shigeyoshi Honda.

Upon returning to Australia I worked through many of the experiments listed in Kado's book, including a set of Limestone Glazes varying alumina and silica. I had been familiar with the volumetric blending technique for a number of years, having got the idea from F.H. Norton's *Ceramics for the Artist Potter*, and I used this labour saving method to make up the set of Limestone Glazes, 35 separate glazes made by blending the four extremes to give (mathematically) a variation of both alumina and silica while keeping the fluxes constant. While working through Kado's experiments I developed the idea of a systematic approach to base glazes taking firstly a modified version of his Limestone Glazes experiment, then replacing half of the lime with barium, magnesium and zinc oxides to produce sets of barium, magnesium and zinc glazes respectively. An important idea here, which I have maintained wherever possible throughout the course, is to change just one thing at a time so as not to confuse the issue when assessing causes and effects.

This systematic approach to base glazes was the basis of the first course I offered to the Queensland Potters' Association in Brisbane in 1979. The course of three hours a week over thirty weeks was well attended and involved theoretical lessons followed by sessions of mixing and applying glazes prepared in sufficient quantity so that all could sample and fire them. A policy of open sharing of information and results was generally adopted by all, and in this atmosphere with the combined energy of the group of more than forty people we began to forge ahead in our understanding of the subject as fired results were brought back for examination week by week. I learned as much as any of the students, much of the work having previously been familiar to me in theory only. I would like to express my gratitude to my many friends in the Q.P.A. who contributed so much to the development of the course.

With the experience gained I was able to propose to the Australian Flying Arts School that I write and conduct a correspondence course to make the material available to all Australian potters. AFAS took up the idea with enthusiasm, and assistance was provided by the Crafts Board of the Australia Council to publish a series of booklets containing the course notes. I designed the 'assessment tile' to enable students to send miniature samples through the mail so that tutors could assess the quality of their work. It soon became evident, however, that the assessment tile with its multiple applications of glazes was a most useful tool in its own right, especially in the early exploratory stages of an experiment, enabling large numbers of glazes to be handled efficiently and because of their relatively small size, enabling hundreds of glazes to be fired together in virtually identical conditions. The use of the assessment tile has now been written into the course as the standard first step in any experiment. The AFAS correspondence course has run successfully from

1980 to the present, giving a solid foundation in glaze technology to hundreds of students around Australia and even overseas.

In 1984 it became desirable to revise some sections to eliminate certain anomalies, and so I decided to rewrite the whole course to incorporate some important improvements and to present it as a book. The original framework of the base glazes sets was altered to what I call the 'baseline grid' approach to include some interesting low silica glazes and exclude some high silica glazes that usually do not melt. Several completely new sets were also included.

At about this time I was shown how useful computers could be; I was sent a series of printouts provided by a student in Sydney showing the recipes for all base glazes in the various sets of the original AFAS course. (Previously students had to calculate these.) I investigated the possible application of computer data processing to the course. I am very grateful to my friend Wendy Archer for showing me how to use a small computer; with her help I have been able to work out programs to eliminate lengthy and troublesome calculations from the course. A series of simple programs was produced enabling all the basic conversions (formula to recipe, formula to oxide weight % etc.) to easily be performed using a basic spreadsheet program called Supercalc. I also obtained a copy of the program that produced the recipe printouts, and an equivalent program using Supercalc was worked out. I was then able with a couple of weeks' work to present all recipes, Seger formulae and oxide weight % figures for all of the base glazes and most of the glazes in Part II as well. This has resulted in an integrated approach to glaze theory, presenting glaze composition in the three usual forms (recipe, oxide weight % and Seger formula) enabling one to have easy access to the data irrespective of one's theoretical background.

This book is now presented as the culmination of this development process presenting:

1. a systematic approach to glaze theory
2. a technique for efficiently preparing and handling large numbers of glazes and
3. ready-worked data (recipes etc.) for all glazes presented in the course.

Special thanks go to my teacher Peter Rushforth for his continuing help, inspiration and friendship, to Shigeo Shiga, whose substantial help towards my studies of Japanese ceramics provided the starting point for this book, and to Shigeyoshi Honda whose patience and generosity contributed greatly to the success of my studies in Japan.

EXPLANATORY OUTLINE

PRACTICAL GUIDE
Read this first for an introduction to the approach presented in this book.

For the Beginner . . . who looks at all the diagrams and words, and says, 'this is too technical for me,' here is a Guide to prove to you that it isn't.

For the Teacher . . . looking for an appropriate framework to teach glazes this will demonstrate the union of theory and practice, and show how to efficiently produce a large range of related fired glazes that are a reference source far more valuable than any book.

For the Experienced Potter . . . with a working knowledge of glazes already, this Guide will enable you to jump right in at the appropriate spot, without having to read through all the more basic material.

The Guide consists of reading the material listed below and performing Experiment No. 3, outlined on page 52. This will take you to the heart of the method presented and used in this volume. It shows the practical technique and how the results relate to the extensive data and theory.

Before the Experiment read the Following Pages:

8- 9...."Guidelines for Selection of Materials."
16-19...."Getting Started — Material Requirements."
21-24...."Volumetric Blending — Lots of Glazes with Little Work."
25-27...."Baseline Grids and Biaxial Blends."
28-33...."Experimental Procedure for Biaxial Blends."
45-47...."Preliminary Comments on Experiments."

You should then be able to perform the experiment.

After the Firing read the Following Pages:

24...."Labelling Test Tiles and Recording Data."
33...."Putting the Results in Order."
35...."Assessment of Results."
36-39...."Effects of Varying Alumina and Silica."
52-53...."Results Charts" and "Comments on Results."
51-53...."Charts" and "Data Sheet."

The following points will then become clear....

1. The 'mass production' of test glazes by volumetric blending and the 'mass handling' by assessment tiles provides a manageable technique to cover large areas of related glazes.
2. Studying sets of related glazes unlocks the door to understanding cause and effect.
3. Combining your fired results with information given in the book provides a unique fusion of theory and practice.
4. The data given in the book unites the three different approaches to studying glazes: recipe, oxide weight % and Seger formula.

BASE GLAZES - A KEY TO UNDERSTANDING GLAZE PRINCIPLES

If we want to really understand why glazes perform as they do, we should start with a study of base glazes, that is, glazes before colourants or opacifiers have been added because many of the qualities that interest potters are explainable in terms of the base glaze alone. Properties such as mattness, shininess, transparency, opacity, opalescence, glaze fit, many colour responses etc. can usually be explained simply by considering the base glaze. Part I of this course presents a systematic approach to base glazes.

From the infinite number of possible combinations, I have selected the range most useful to the stoneware potter and varied alumina, silica, a number of fluxes, and the firing in a way that allows the student to isolate one variable at a time and see the effect it has on a glaze.

LIMITS

The useful limits of the experiments are to some extent determined by the temperatures used, and to some extent by the raw materials. Diagram 1 shows the limits of alumina and silica for the 8 sets of glazes studied here in detail, and the composition of the fluxes for each set is set out below.

At this point I will quote 'molecular parts' (M.P.) only because the substitutions giving the different sets are done on a molecular parts basis, but when dealing with the actual glazes later, I will also give oxide weight % and recipes. Each 'set' consists of a group of 35 glazes all having the same set of fluxes but with alumina and silica varying systematically over a broad range as indicated in Diagram 1.

The glaze sets are named according to the predominant flux used in each. The first four sets have fluxes that lie on a line blend between limestone and K-feldspar:

0.9 Limestone Set	**0.8 Limestone Set**
0.1 K_2O	0.2 K_2O
0.9 CaO	0.8 CaO

0.6 Limestone Set	**0.6 Feldspar Set**
0.4 K_2O	0.6 K_2O
0.6 CaO	0.4 CaO

A further three sets are obtained by taking the 0.8 Limestone Set and replacing 0.5 M.P. of the CaO by 0.5 M.P. of either MgO, BaO or ZnO:

Magnesium Set	**Barium Set**
0.2 K_2O	0.2 K_2O
0.3 CaO	0.3 CaO
0.5 MgO	0.5 BaO

Zinc Set

0.2 K_2O
0.3 CaO
0.5 ZnO

The final set is obtained by replacing the remaining 0.3 M.P. of CaO in the Barium Set with lithium oxide, to give:

Barium-Alkaline Set

0.2 K_2O
0.3 Li_2O
0.5 BaO

METHODOLOGY

1. Materials and Glaze Calculations

All calculations for the sets of base glazes are done using theoretical formulae for raw materials. For this approach to work well, one must take care in selecting the raw materials used. (See 'Guidelines for Selection of Materials Page 8'.) Once this is done, however, one is then able to apply a vast amount of computer processed data presented here, virtually eliminating the need for calculations in Part I of the course. Nevertheless, a section on glaze calculations is given for those wishing to cut new ground using this approach or simply to understand the subject better.

It should be noted here, however, that the main reason for using pure materials for the base glaze experiments is not for the convenience of computer processed data, but to eliminate extraneous variables as much as possible from the ingredients.

2. Preparation of Glazes

Any one set contains 35 glazes, for example the 0.8 Limestone Set is illustrated in Diagram 2, each dot representing one glaze. The 35 glazes are produced by the volumetric blending technique - in brief, this consists of making up the four 'corner glazes'

marked A,B, C and D, and blending them in liquid suspension to give the remaining 31 glazes in the set, this technique being far more economical of time and materials than weighing out each glaze individually.

3. Application of Glazes

In any one set all 35 glazes are applied to one large tile, an 'assessment tile' (about 100mm x 150mm), in the same 5 by 7 layout as shown in Diagram 2. One is able, therefore, to see at a glance how the fired results relate to the alumina/silica diagram. Anything from 5 to 10 identical assessment tiles are prepared from each set of 35 glazes, these to be fired under different conditions. For the initial investigations, the assessment tiles are made of an iron-free clay such as a porcelain or a fine white stoneware; subsequent studies may make use of different clay bodies and larger test pieces for individual glazes.

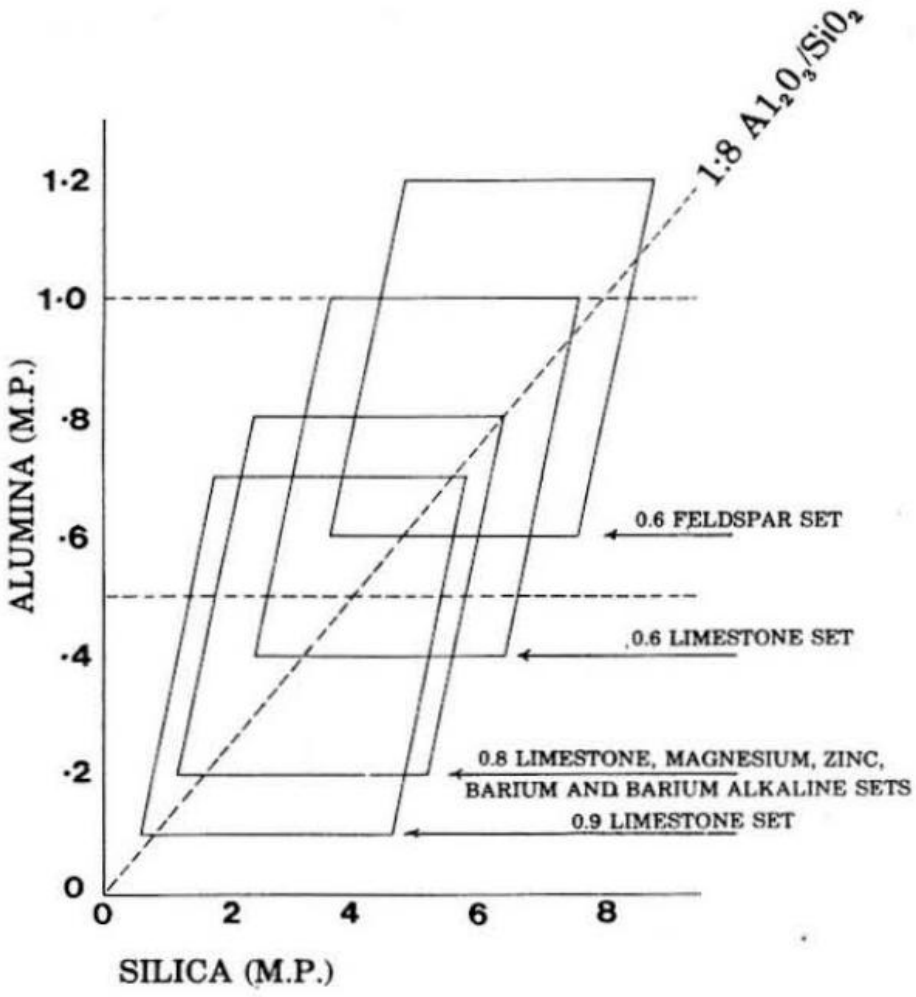
4. Firing

For exploratory work, one can fire the tiles any way one pleases. There is much to be learned, however, from firing all 8 sets of glazes under identical conditions and to repeat this over a range of temperatures, kiln atmospheres, rates of cooling etc. The tiles are meant to be fired horizontally, so 8 assessment tiles, one from each set, can be fired in a stack taking up about the volume of a standard brick or less. As long as the stack is fired in a zone of uniform pyrometric conditions, one can consider all 280 glazes to be fired under virtually identical firing conditions. This yields a lot of very useful comparative data.

5. Results

Fired results will vary a little from one potter to another, depending on raw materials, firings etc., and as long as the experiments are done with care, the

DIAGRAM 1: Limits of Alumina and Silica for the various sets of Base Glazes.



results produced by the individual in his/her own kiln are the most useful. Typical results are given here from tests of my own and of students, to give a guideline as to what to expect and to provide examples to explain the broad range of glaze phenomena that are determined by the base glaze. These typical results are plotted onto diagrams using the same format as Diagram 2 and fleshed out with verbal comments.

6. Data

Data Sheets are provided for each set of glazes, giving Seger Formula, Oxide Weight %, and one or more typical recipes for each glaze. To enable one to better understand the relationship between these three different ways of expressing glaze composition, the Data Sheet information is also presented graphically in the 'Oxide Weight Charts' and the 'Recipe Charts'.

Data Sheets are also given for sets of glazes not done in this course but which lie intermediate to the 8 sets that are covered.

7. Text

The general text is the basis of the Australian Flying Arts School Correspondence course in Stoneware Glazes and is, therefore, fairly detailed to minimise the amount of queries to the tutors. Where some basic aspect of glazing is adequately covered in a standard available text, I have simply referred the student to that author. See under 'Reference Books' in the 'Introduction' in the following pages.

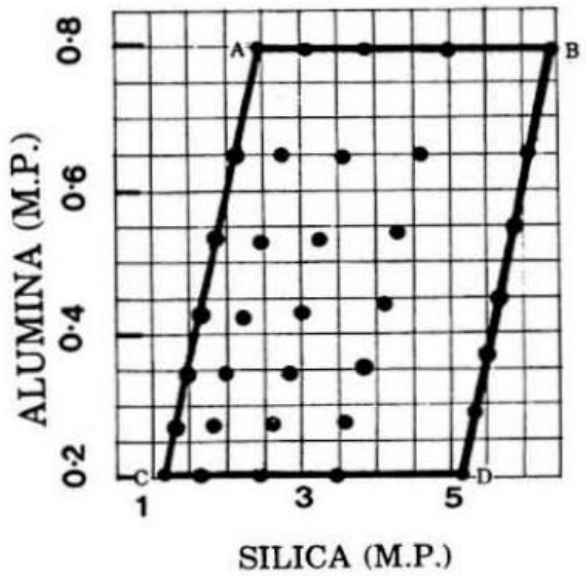
8. Calculations

For all of Part I (Base Glazes) and most of Part II, the calculation of recipes, oxide percentages etc. have already been done and are presented in the Data Sheets. There is much about stoneware glazes, however, that lies beyond this course; and if you want to explore uncharted lands, you will need to learn how to navigate. See the chapter on 'Calculations'.

9. Part II

Whereas Part I takes a divergent approach to glazes, showing a technique to gain an overview of the whole field, Part II takes the convergent approach, focusing on individual glazes and glaze types, both traditional and modern.

DIAGRAM 2: 5 x 7 Layout of Blended Glazes.



PART 1

BASE GLAZES

1 PREPARATIONS

INTRODUCTION

After five years of development with hundreds of students around Australia and elsewhere, this course has now reached an interesting stage. It is still presented as a course on high temperature glazes, but the 'baseline grid' approach used here can be applied to glazes for any temperature, and the volumetric blending technique enables large numbers of related test glazes to be prepared with a minimum of time and expense. Also the use of 'assessment tiles' allows 35 glaze samples to be handled as easily as one; and they allow hundreds of glaze samples to easily be fired in virtually identical conditions, enabling comparisons to be made in the knowledge that observed differences are not due to differences in firing. The volumetric blending process, producing many related glazes by careful blending of four extremes, by its very nature allows easy computer data processing to produce recipes for all the glazes by inputting the recipes of the four extremes. Using this technique, the recipes and oxide weight % figures for all the glazes used in the course have been worked out on computer and presented here along with Seger formulae. In fact, the computer has eliminated the need for doing calculations in most of this course, but the calculations techniques are nevertheless explained for anyone wishing to break new ground.

This is meant to be a practical course with just enough theory to enable you to produce the fired results; the ultimate teaching aid here is not this book but the fired sets of related glazes it helps you produce. Those people actually doing the experiments will get much more out of this book than those who use it to guide them in stabbing for desired effects with spot tests. But if spot tests are all you have time for, the 'Results Charts' and the 'Comments on Results' will give useful guidance.

If you want to get the most out of this course, some work is required. The kernel of Part I, the sets of base glazes, will take one person working carefully and efficiently about forty hours -- about five hours per set — to the stage where five to ten 'assessment tiles' of each set are ready to go into the kiln. It takes much less time if done with a group. Part II might take a week or a lifetime, depending on how deep you want to go.

GROUP STUDY

The original version of this course was run in Brisbane at the Queensland Potters' Association, and this experience showed quite clearly that the group study approach has much to recommend it. Some of the advantages are:

1. You can divide the workload with different people doing different experiments or different parts of the same experiment, making sure that quantities are sufficient so that all students can get samples of all the test glazes.
2. With several people firing samples of the same sets of glazes in different kilns, one will get a better appreciation of the effects of different firing cycles, temperatures, kiln atmospheres, rates of cooling etc.
3. By arranging a fixed time for the group to meet each week, you will find it easier to get down and do the work, than if you rely on doing it yourself 'when I have the spare time'.
4. In a group, you will find that different people have different skills. If you intend working through the chapter on calculations, some will find it easy to understand and be able to explain it to others.

REFERENCE BOOKS

Those of you already well used to glazing and firing your own pots will probably not need much extra reading apart from this book. For beginners, I will often be referring to standard texts that cover the real fundamentals, such as how to mix your glaze and apply it to the pot etc. I have avoided trying to make this book all-encompassing: the assumption is that readers own or can get access to other excellent texts that cover the basics. Students doing the AFAS correspondence course are recommended to get *Glazes for the Craft Potter* by Harry Fraser (Pitman) as a reference for beginners, and Frank Hamer's *Potter's Dictionary of Materials and Techniques* (Watson-Guptill) is recommended as an excellent general reference. Other classics by Leach, Cardew and Parmelee are referred to regularly in the text. In Part II, *Those Celadon Blues* by Robert Tichane (available from him, c/o New York State Institute for Glaze Research, 511 N. Hamilton Street, Painted Post, New York 14870, USA) and also *Oriental Glazes* by Nigel Wood (Pitman) are recommended in the study of oriental glazes.

BASIC GLAZE THEORY AND PRACTICE

As you probably know already, most glazes contain fluxes, alumina and silica. A glaze of this sort is called a 'base glaze' and may be used by itself as a glaze, or it may be altered by adding colouring oxides, and/or opacifiers. In Part I of this course we will be examining a large range of base glazes — eight sets in all — each set choosing a different set of fluxes, and varying alumina and silica over a large range.

At this stage, if you feel a little lost by terms such as *fluxes, alumina* and *silica*, then I recommend a crash course on glaze elements -- either the first four chapters of Fraser's book or reference to Hamer's *dictionary* mentioned above, should help. But in a nutshell: the silica is what makes the 'glass' in the glaze (it is nature's commonest glass former); the fluxes make the silica melt at a reasonable temperature (by itself, silica melts at 1713°C while we are working around 1280°C); and the alumina is the 'stiffener' that makes the glaze viscous so that it does not run off the pot like water as soon as it melts.

For the eight sets of glazes, we will use fairly pure ingredients so that the effects we want to observe are not masked by impurities in the glaze or clay. Base glazes are theoretically free of colouring oxides, but a fairly common impurity in clay is iron oxide that can impart a definite colour to a glaze, even when present only in the clay body in quite small quantities. In choosing the clay body to receive the glazes and in choosing the China clay (kaolin) for use as a glaze ingredient, we will select clays as low as possible in iron oxide.

You must not think, however, that 'purity' equals 'quality'. Often the reverse is the case. Purity aids understanding by removing some of the unforeseeable variables. Your pure materials will better show the influence of the variables you have chosen to examine; and once you understand how these variables work, you can then apply these principles to less pure materials with understanding. Once the experiments have been done, I will actually recommend that less pure materials (less expensive and more readily available) are used to produce equivalents or derivatives of the experimental glazes for general use in your pottery workshop.

For those new to pottery who have not had much experience at actually getting a glaze onto a pot, I recommend you read Chapters 14 and 15 in Fraser's book. But here are the basic points:

1. Care should be taken with powdered glaze materials. Barium carbonate is poisonous, and some materials are dangerous if inhaled, especially silica.
2. You need a set of scales that will weigh fairly accurately up to about a kilogram. If it measures to a tenth of a gram, that should be as accurate as you need for most applications. If you are using cheap scales, you should get them tested by putting some accurate weights on the pan.
3. We will not be using a hydrometer or glaze binders or electrolytes as mentioned in Fraser (Chapter 14) but will use clay (usually kaolin) as a suspender wherever this is acceptable by the glaze formula.
4. The main methods of glaze application will be by syringe and by dipping.
5. You will need to get the feel for what is adequate thickness for glaze application. We will be using variations in thickness to learn as much as possible from each tile. More on that later.

RAW MATERIALS

In this section I will deal with some of the peculiarities of commercially available raw materials. But before I start, I wish to remind you (to maintain a balanced perspective) of the wealth of raw materials to be had in Australia just by going out and digging your own. Apart from the escallating cost of the commercial product, the satisfaction of winning your own materials, plus the individuality it gives to your work, makes it a most fruitful alternative to getting everything out of a bag. If you are so inclined, the following books are most useful:

Pioneer Pottery by Michael Cardew (Longman Cheshire).

Notes for Potters in Australia - Raw Materials and Clay Bodies by Ivan McMeekin (New South Wales University Press).

See also Chapters 4, 25 and 26.

Reliability

The various ingredients that you use in your glazes and clay bodies are freely available from pottery suppliers in Queensland and interstate. The rapid growth in popularity of craft pottery over the last ten years has made it profitable for businesses to specialise in pottery materials and equipment, but it is still early days yet, and the pottery suppliers have still a lot to learn. We have to be aware of the limitations of what they are able to do, especially as regards supply of reliable materials.

When you buy a bag of feldspar or kaolin etc., you should be able to get an analysis sheet telling you exactly what the bag is supposed to contain and the amount of variation you can reasonably expect. Usually the best you can obtain in Australia is a 'Typical Analysis' with no indication of how much your bag is likely to vary from the 'typical', and certainly no guarantee that the typical analysis bears any relationship whatsoever to what you have bought. In the last ten years, I have had two bags of 'feldspar' that were simply not feldspar, and I have heard of other similar cases. Upon returning the faulty material to the rock miller, I was told, 'Sorry about the hundreds of dollars of ruined pots... here is another bag of feldspar'. But I was not told what had been in the original bag, or how it happened, or what likelihood I had of winning the dud-bag lottery at a later date. I should point out that this is not a very common occurrence, but probably most potters will come up against it sometime, so I will list a few points to help you prevent what is potentially a major disaster in any workshop:

1. Ask for an analysis sheet — especially if you are buying a whole bag (25-40 kilos).
2. Order well before you need the new materials so you can test on a small scale before large scale use. A small test kiln is useful if you want to test materials in a hurry and your only other kiln is very large.
3. Buy big lots if possible. If you are a full-time potter, or if your group can afford it, there are economies and conveniences in buying, say, a mixed tonne of glaze and clay materials direct from the wholesaler. Buying in this way, if you were to buy ten bags of feldspar for example, chances are that the bags would be identical; a visual and tactile examination alone is enough to reassure you that the next bag is the same as the previous. I have never heard of anyone getting a whole dud batch — and dud bags usually look and feel suspect.
4. Buy directly from the rock miller if possible, and in person. This way you can talk with the technical expert about analyses of the materials, get analysis sheets, get some idea from the horse's mouth on how accurately the analysis sheets will relate to the contents of the bags you are buying; and you will be able to see their full range of materials that will include things you have never heard of and pick up a few free samples. If you are interested, you can usually find out also where the different minerals are mined.

Analysis Sheets

You should be able to obtain these from your suppliers or directly from the mineral wholesaling company. It is usually a single sheet containing a detailed physical and chemical analysis of the particular material in question. On this sheet will usually be a 'Typical Chemical Analysis' or 'Typical Analysis', which lists the usual quantities of the various oxides present in weight percentage. In the chapter on 'Calculations' I will show you how to convert this list of percentages into a molecular formula with its molecular weight; but in most cases, we will be able to use the theoretical molecular formula instead of the actual since there will often be not much difference between the two.

It is useful to be able to form a rough idea of the purity by looking at the analysis sheet, and without having to convert the % figures to molecular formula. To help you do this, I have listed in Table 1.1, a number of theoretical analyses for theoretically pure materials. By comparing the actual Typical Analysis with this theoretical analysis, you can see how close it comes to the theoretical formula that you use in your glaze calculations. I have also listed some typical analyses for your comparison.

Variations in Raw Materials

Here are a few comments on variations you can expect to find in your normal bagged materials obtained from your pottery supplier or mineral supplier:

1. **Feldspar and Other Alkali Fluxes**

The main reason we use feldspar in glazes is that it provides a cheap source of insoluble alkali fluxes (K_2O, Na_2O). Theoretical potash feldspar has 16.9% K_2O, and theoretical soda feldspar has 11.8% Na_2O.

Impruities in your bag of feldspar will probably reduce this percentage, and therefore reduce its effectiveness as an alkaline flux; but with most commercial feldspars, the effect is only marginal. (The picture is complicated a little by the fact that your bag of feldspar always contains more than one type of feldspar. 'Potash feldspar' often contains around 20% soda feldspar, and your bag of 'soda feldspar' will usually contain some potash spar plus some calcium feldspar (anorthite). However, by looking at the theoretical composition, and comparing the 'Typical Analysis' with it, you should be able to get a good idea of how pure and how suitable the material is to your need, assuming that the typical analysis is reasonably accurate.

In a bag of potash feldspar (which is what we normally use for feldspar), the main non-feldspathic impurity is a little quartz (SiO_2) resulting from the fact that it is economically impossible to separate the quartz and feldspar crystals completely when it is mined. So your 'Typical Analysis' will show slightly high SiO_2, and slightly low KNaO (see below). Incidentally, if you gather feldspar yourself from a local pegmatite outcrop, you can usually select pure feldspar crystals, excluding any quartz. (If you are interested, ask a local geologist about feldspar from local pegmatite, especially if you have granite in your area.)

'Accessory minerals' with the feldspar are responsible for the small quantities of other oxides (MgO, Fe_2O_3, CaO, TiO_2 etc.).

Note: KNaO

This term means 'K_2O and/or Na_2O' and is used because:

a. in many cases it is irrelevant whether we use K_2O or Na_2O or a mixture of the two, and

b. in most cases the raw material we use to provide the K_2O or Na_2O (e.g. K feldspar) is actually a mix of the two. So if you usually use K feldspar when you see a formula calling for KNaO, you can read it as K_2O, or if you wish for some reason to use Na feldspar, read it as Na_2O.

Other Alkaline Fluxes:

If you wanted to make a glaze of the following composition:

$$\begin{matrix}0.8\ KNaO \\ 0.2\ CaO\end{matrix} \quad 0.9\ Al_2O_3\ 4.0\ SiO_2$$

you will find it is impossible to use feldspar alone to provide all the alkaline fluxes because if we introduce 0.8 M.P. (molecular parts) of KNaO by using 0.8 M.P. of feldspar, this automatically introduced $0.8 \times 6 = 4.8$ M.P. of SiO_2, which is more than required. In this case, you could use nepheline syenite to get out of trouble since it has a lower proportion of silica, usually about 4.2 to 4.9 M.P. of SiO_2 for every 1.0 M.P. of KNaO. It is fairly variable (note the two different formulae given on pages 31 and 139 of Fraser and also four analyses and formulae on page 55 of Cardew's *Pioneer Pottery*) so you will need to use the Percentage Method of calculation or work out the molecular formula and molecular weight from the typical analysis (see Chapter 14).

If you want a very alkaline glaze with very low alumina or silica, you will find that you probably need to go to using a commercial alkaline frit, which is produced especially to solve this problem. The analyses are usually available where the frit is sold and are very accurate. Two alkaline frits generally available in Australia are:

TABLE 1.1: Theoretical and Actual Analyses of Some Common Raw Materials.

	FELDSPARS				KAOLINS				BALL CLAYS				TALCS		DOLOMITE
	Potash (K)		Soda (Na)			Russell Cowans			Russell Cowans		Wengers				
	Theoretical	Russell Cowans	Theoretical	Russell Cowans	Theoretical	K1 (Airflo)	Eckalite	K50	China Clay No. 2 1113W	QA	C	No. 1	No. 3	Theoretical	Wengers Talc	Theoretical
K_2O	16.9	10.3		0.2		0.2	0.26	0.3	1.84	1.0	0.3	2.5	2.47			
Na_2O		3.6	11.8	10.6		1.0	0.06	0.3	0.08	1.0	0.2	0.4				
CaO		0.3		1.1		0.5	0.05	0.2	0.10	0.3		0.2	0.14		0.21	30.4
MgO		0.1		0.2		0.1	0.01	0.2	0.25	1.0		0.4	0.5	31.8	32.13	21.9
Fe_2O_3		0.3		0.2		1.0	0.75	1.1	0.6	0.9	0.7	1.0	0.92		1.66	
Al_2O_3	18.3	18.0	19.4	20.0	39.5	35	38	30.3	37.2	27.0	28.4	32.6	21.0		7.13	
SiO_2	64.8	67.0	68.8	67.2	46.6	48	46	51.1	47.7	57.2	57.1	52.9	67.0	63.6	51.8	
TiO_2						1.1	0.66	1.2	0.03	1.5	1.0	1.0	1.5		0.28	

Podmores P 2250 High Alkali Frit

0.5 Na_2O		1.5 SiO_2
0.3 K_2O	0.1 Al_2O_3	0.1 B_2O_3
0.2 CaO		

Molecular Wt 176

Ferro Frit 3110

0.064 K_2O		3.30 SiO_2
0.643 Na_2O	0.10Al_2O_3	0.10 B_2O_3
0.291 CaO		

Molecular Wt 271

I suggest you insert these formulae and molecular weights in your Table 14.1 (Chapter 14) List of Raw Materials.

2. Kaolin and Other Clays

Kaolin (China clay) is a product that we sometimes require to be very pure. In the case of glazes this purity is important when whiteness or lack of colour is desirable, and we must therefore minimise Fe_2O_3 content. Sometimes the presence or absence of small quantities of subsidiary oxides (especially TiO_2 and P_2O_5) will have a marked effect on the quality of traditional Chinese glazes. (See Nigel Wood's *Oriental Glazes*, pages 46, 47 etc.).

Starting with pure (theoretical) kaolinite ($Al_2O_3.2SiO_2.2H_2O$), with a breakup (% by weight) of 39.5% Al_2O_3 and 46.6% SiO_2 (the balance of the 100% representing the two molecules of water per molecule of kaolin) we will find that as kaolins become less and less pure, the Al_2O_3 % will fall, the SiO_2 % will rise, and the amount of subsidiary oxides (e.g. CaO, Fe_2O_3, TiO_2, K_2O, Na_2O, MgO etc.) will rise.

Comparing the various kaolins in Table 1.1, you will see that of those listed, eckalite and Wenger's kaolin No. 2 are the purest, and K50 the least pure. But bear in mind my comments at the beginning of this course that purity of raw materials does not necessarily equate with quality in the end product.

Ball clays are very variable in composition, and so it is not possible to put up a general molecular formula and molecular weight. If you want to use ball clays in your recipes using the molecular formula approach with any degree of predictability, then you will have to use the Percentage Method, or work out the molecular formula and molecular weight for each ball clay that you use, working from the typical analysis. (See Chapter 14) But generally speaking, your ball-clay analysis will reveal considerably less Al_2O_3 and more SiO_2 than kaolins and a significant presence of fluxes, iron and titanium oxides. See Table 1.1.

Other clays, such as fireclays, terracottas, impure kaolins etc. all have a place in our list of glaze materials (as well as having a use in compounding clay bodies); but as with the ball clays, to use them in glaze calculations, you will need an analysis. However, you can use them without an analysis if using an empirical approach as we use in the ash/clay/rock glazes.

3. Whiting

Most whiting produced by Australian rock millers is very pure, being almost pure calcite, typically over 98% $CaCO_3$. If you want to use local sources of lime, of which there are plenty available, you will often be dealing with a much less pure product.

4. Dolomite

These minerals are notoriously variable. The theoretical formula is $CaCO_3.MgCO_3$. However, the molecular proportions of the two sub-molecules is usually not 1:1 as the formula would suggest, and impurities are present. Also it may be difficult or impossible to get an analysis for a particular dolomite. By all means use local dolomites in your glazes, but if you want to use it as a predictable ingredient in your glaze calculations, you should use a dolomite for which you can get a reliable analysis, or use one of the other sources of MgO in your glazes.

5. Talc

You can usually use the theoretical formula when using talc in your calculations (i.e. $3MgO.4SiO_2.H_2O$). The talc I use (Micromist Talc TX15) has the formula: $3MgO.0.14Al_2O_3.3.6SiO_2.1.36H_2O$. with a molecular weight of 376. Also there are small impurities of Fe_2O_3, TiO_2 and CaO. Once again, I suggest you get the analysis sheet for your talc and compare it with the theoretical percentages given in Table 1.1.

6. Magnesium Carbonate and Magnesite

Light $MgCO_3$ is very pure but tends to cause crawling if used in large quantity in the glaze batch. Heavy $MgCO_3$ (ground magnesite) is not so pure (usually containing a little Fe_2O_3) but does not

cause crawling However, cobalt purples seem to be favoured by the light form. Also there are other slight differences between glazes using the different forms of $MgCO_3$.

7. Colouring Oxides

In general these are fairly pure, but recently some potters have had problems with an iron oxide being sold in Queensland. By what I have heard it seems that the product is more of an ochre than a reasonably pure iron oxide. An ochre is iron oxide with substantial quantities of clay. This sort of thing would usually not be a bother if one only had an analysis of the material since one could then adjust the recipe percentage accordingly.

References

The best pottery text to read on raw Materials is Cardew's *Pioneer Pottery*, Chapters 2, 3, 4 and 5. Also read the text by Fraser, Chapter 6.

If you wish to win your own raw materials, the best texts are:

Notes for Potters in Australia - Raw Materials and Clay Bodies by Ivan McMeekin (New South Wales University Press), and once again, *Pioneer Pottery*.

Technical Notes for the Craft Potter, available from Russell Cowan Pty Ltd, contains numerous molecular formulae and typical analyses for materials commonly used in Australia.

The newly published *Handbook for Potters in Australia*(Methuen) by DeBoos, Harrison and Smith contains a list of analyses of materials commonly available from pottery suppliers. See their Appendix 8.

GUIDELINES FOR SELECTION OF MATERIALS

All the glaze calculations for the base glazes are done using the formulae for theoretically pure materials. Therefore, the materials used must be reasonably pure, so care is needed in their selection.

Glaze Materials

There are actually only eight raw materials used in the base glazes presented in Part I, selected as a compromise between purity and relevance to normal glaze practice, i.e. I have tried to use materials that are commonly used in stoneware glazes, but I have eliminated some potential sources as being too variable or too impure.

Silica, lithium carbonate, calcite (whiting), barium carbonate and zinc oxide are easily obtained in an adequately pure state, e.g. 98-99% pure. The source of magnesia recommended is 'light' magnesium carbonate; 'heavy' grade is all right at a pinch, but it contains significant impurities and gives a slightly different result.

Kaolin: Careful selection of the kaolin used is important, as many kaolins contain significant amounts of iron and titanium oxides, which will affect the results. However, there are some very pure kaolins generally available -- it is just a matter of checking the analysis and knowing what to look for. As an example, I have listed below the analyses of three kaolins, for comparison. The Wengers Kaolin No.2 is one of the purest commercially available in Australia, and is excellent. Kaolin K50 is really too impure, with significant iron, titanium and extra silica.

Two other kaolins that are suitable and generally available in Australia are: Eckalite No.2 and Grollegg China clay.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2 %	MgO	CaO	K_2O	Na_2O	Ignition Loss
Pure Kaolin	46.6	39.5	—	—	—	—	—	—	13.9
Wengers 2	47.7	37.2	0.6	0.03	0.25	0.10	1.84	0.08	?
Kaolin K50	55.1	30.3	1.1	1.2	0.2	0.2	0.3	0.3	11.3

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Pure K-Feldspar	64.8%	18.3%	—	—	—	—	16.9%
Steetley 200FPR	66.0%	18.0%	0.2%	—	—	3.0%	12.0%
Steetley 200F	67.5%	18.0%	0.12%	0.4%	.08%	3.5%	9.8%

Feldspar: the calculations are based on theoretically pure potash (K) feldspar, but this is virtually never available commercially. Adequately pure feldspars are widely available commercially in Australia, however, such as Steetleys Potash Feldspar Premium 200 FPR and their Potash Feldspar 200F. The analyses are given along with the theoretical analysis of pure K feldspar. Some soda (Na) is virtually unavoidable in commercial K feldspars; in general, the points to consider are:

1. maximise K_2O ($+Na_2O$)
2. minimise excess SiO_2 (ideally 64.8%)
3. minimise Fe_2O_3 and
4. minimise CaO, MgO and other impurities.

ANALYSES OF ACTUAL MATERIALS USED

When selecting the raw materials to make up the base glaze sets from which the Results Charts were drawn up, I obtained the following 'typical chemical analyses' from the suppliers:

Potash Feldspar.

SiO_2 66.0%; Al_2O_3 18.4%; Fe_2O_3 0.3%; CaO 0.3%; MgO 0.1%; Na_2O 3.2%; K_2O 11.3%; Ignition Loss 0.4%

Lithium Carbonate.

99% Li_2CO_3

Whiting (Circal 60/12).

$CaCO_3$ 98.5%; $MgCO_3$ 0.6%; Acid insolubles 0.5%; Fe_2O_3 0.04%; Al_2O_3 0.1%; SiO_2 0.3%

Magnesium Carbonate (Light).

MgO 42.05%; Ignition Loss 54.65%; CaO 0.32%; Fe_2O_3 + Al_2O_3 0.07%; Insoluble matter in HCl 0.07%; Soluble matter in Water 1.02%; Moisture 1.82%.

Zinc Oxide.

99.9% ZnO

Barium Carbonate.

99% $BaCO_3$

Kaolin (K37).

Ignition Loss 13.6%; SiO_2 45.9%; Al_2O_3 39.0%; Fe_2O_3 0.4%; CaO 0.4%; MgO 0.3%; Na_2O 0.1%; K_2O 0.1%; Cu 3 ppm.

Silica.

SiO_2 99.5%; Fe_2O_3 0.06%; Ignition Loss 0.18%.

Clay Bodies

All initial tests are done on fine iron-free stoneware or porcelain tiles. Podmores porcelain is excellent, and Morlynn porcelain is also adequate. After initial testing on the fine white body, the student is encouraged to try other clays.
See also the previous section, 'Raw Materials'.

U.S.A. and U.K. Kaolins and Feldspars

For potters in the U.S.A. or Britain, there are many kaolins and feldspars suitable for use in the base glaze sets. Some analyses are reproduced below.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	L.O.I.
Grolleg Kaolin	48	37	0.7	0.02	0.06	0.3	1.85	0.1	12.2
E.P.K. China Clay (Florida)	45.91	38.71	0.42	0.34	0.09	0.12	0.22	0.04	14.16
Potterycrafts Potash Feldspar P.3296	65.8	18.5					12.0	2.92	
Kingman Potash Feldspar	66.5	18.4	0.08	—	0.10	Tr.	12.0	2.7	0.2
Keystone Potash Feldspar	64.76	19.94	0.04	—	0.17	—	12.24	2.48	0.35

2 BASIC CHEMISTRY

Because all the glaze recipes are presented in the text, it is not necessary to understand this chapter before proceeding to the experiments that make up the core of Part I. This section is easy to understand, however, even for someone lacking confidence in mathematics and unfamiliar with chemistry, and this understanding will help readers to better grasp the theoretical basis of this course and enable them to use the method to design their own experiments outside the limits presented here.

The main thing I want to do at this stage is to explain enough basic chemistry for the reader to understand the relationship between the Seger formula, the glaze recipe and the oxide weight %. We need to start by considering atoms.

ATOMS

All matter is made up of atoms. There are about a hundred different types of atom, and they are the chemical building blocks of the universe. Usually they are bonded together with other atoms of the same kind or different kinds to make chemical compounds; and when a chemical reaction occurs, what is happening is that the bonds are broken and/or new bonds are formed, producing new chemical compounds. For example, when you heat whiting in your kiln, the chemical compound that is the main ingredient (calcium carbonate) breaks down in a chemical reaction to form two other chemical compounds, namely calcium oxide (quicklime) and carbon dioxide (a gas).

TABLE 2.1 - Short List of Elements

Element	Symbol	Atomic Weight (Approximate)
Aluminium	Al	27
Barium	Ba	137
Boron	B	11
Calcium	Ca	40
Carbon	C	12
Hydrogen	H	1
Lithium	Li	7
Magnesium	Mg	24
Oxygen	O	16
Potassium	K	39
Silicon	Si	28
Sodium	Na	23
Zinc	Zn	65

So chemical reactions occur in the raw materials of the glaze during the firing, and because of this we must understand a little about atoms — the building blocks that are juggled around in chemical reactions — if we want to understand the process more fully.

Table 2.1 is a list of the main atoms or 'elements' that you will be using in this course. For a more comprehensive list, see a standard text, such as Hamer or Fraser. The atomic weight is the weight of the atom, not in grams or pounds or whatever, but in relation to the weight of one atom on hydrogen, which is given the arbitrary atomic weight of 1 unit. (Hydrogen is the lightest of all the elements and so it is an appropriate choice as the standard.) For example, aluminium has an atomic weight of 27, which means that one atom of aluminium is 27 times heavier than one atom of hydrogen.

MOLECULES

In nature, most atoms are unstable by themselves, and they join together with other atoms of the same kind or of different kinds, to form molecules. Any pure chemical compound is made up of vast numbers of molecules of the same kind. And again, we are interested in their 'weight', this time called the 'molecular weight'. In the following list, I have put most of the molecules you will have to deal with for this course, along with their chemical formula, and molecular weight. You will find a very comprehensive list of chemicals in Hamer's *Dictionary* or Fraser's Appendix 10. But first a few notes of explanation:

a. Let us use whiting again as an example to explain how you read the formula. We will assume it is pure calcium carbonate. The formula for one calcium carbonate molecule is $CaCO_3$.

b. Note that the molecular weight is the sum of the individual atomic weights. Take whiting again (using the approximate atomic weights given above).

Formula	:	Ca	C	O_3
Atoms	:	1	1	3
Atomic Weights	:	40	12	16
Molecular Weight	:	(1x40) + (1x12) + (3x16) = 100		

c. A note on compounded molecules:

If you look at the formula for feldspar, talc, China clay, etc., you will see that they

TABLE 2.2 — Short List of Chemical Compounds

Name	Molecular Formula	Molecular Weight
Alumina	Al_2O_3	101.9
Boric Oxide	B_2O_3	69.6
Calcium Carbonate	$CaCO_3$	100.1
Calcium Oxide	CaO	56.1
Carbon Dioxide (Gas)	CO_2	44
China Clay	$Al_2O_3.2SiO_2.2H_2O$	258.1
Feldspar (Potash)	$K_2O.Al_2O_3.6SiO_2$	556.5
Feldspar (Soda)	$Na_2O.Al_2O_3.6SiO_2$	524.3
Kaolin	See China clay	
Potassium Oxide	K_2O	94.2
Silica (Quartz)	SiO_2	60.1
Talc	$3MgO.4SiO_2.H_2O$	379.2
Water	H_2O	18
Whiting	See Calcium Carbonate	

are represented as a mixture of 2 or more 'sub-molecules'. For example, talc ($3MgO.4SiO_2.H_2O$) is represented as a combination of magnesium oxide (MgO), silica (SiO_2) and water (H_2O) in the ratio of 3:4:1. This is a molecular ratio (i.e. 3 molecules of MgO to 4 molecules of SiO_2 to 1 molecule of H_2O) which is different from the weight ratio (i.e. the weight of MgO to the weight of SiO_2 etc.). The full stops '.' in the formula mark the division between one sub-molecule and the next, and the big number in front of the sub-molecule refers to that sub-molecule only, up to the next full stop. If there is no big number in front of a sub-molecule, interpret this as '1'. For example, potash feldspar — $K_2O.Al_2O_3.6SiO_2$. This is potassium oxide, alumina and silica in the (molecular) ratio of 1:1:6.

These are idealised formulae, but are adequate for our purposes as long as we choose reasonably pure raw materials. The list above is meant specifically for this Chapter. See also the 'List of Raw Materials' (Table 14.1) which is designed for use always in your calculations.

OXIDES

Somebody once defined ceramics as the 'science of oxides'. You will find this to be a relevant definition in this course. Sometimes you will be putting carbonates (as opposed to oxides) into the glaze, but the effect of the firing is to turn carbonates into oxides with the carbon going up the chimney as carbon dioxide. If you want to see the molecular formulae of typical oxides and carbonates (to clarify the concepts in your head), see Table 2.2. But whatever you do, read on. The chemical reaction involved in the breakdown of a carbonate in the kiln can be expressed as follows for calcium carbonate:

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2$$

Calcium carbonate breaks down with heat to give calcium oxide and carbon dioxide. In this reaction equation, you will note that both sides of the equation (i.e. on either side of the arrow) contain one calcium atom, one carbon atom and three oxygen atoms, this reflecting the fact that matter cannot be created or destroyed in a chemical reaction. But the main point I am trying to get across now is that after the firing, what you have left in your fired material is an oxide, or group of oxides. The reason for this is simply that you have heated the materials to a very reactive temperature in the presence of oxygen (in the air) so that the materials 'oxidise'. The main exception to this is when you 'reduce' the kiln, i.e. firing with a certain amount of carbon monoxide in the kiln, and the carbon monoxide removes some of the oxygen from some of the oxides. In an extreme case you may end up with the oxide being reduced right back to the metal, for example copper oxide under strong reduction may be reduced to metallic copper, this being responsible for some copper-red glazes. However, for the purpose of our calculations, our glaze mixtures will produce only oxides.

Classification of Oxides

We usually classify the oxides in the following way:

Basic Oxides	Amphoteric Oxides	Acidic Oxides
(fluxes)	(intermediate)	(glass formers)

The various oxides will go into one or other of these three categories, depending on the ratio between 'R' and 'O', where 'O' is *oxygen*, and 'R' is *something* . . . and RO, R_2O, R_2O_3, RO_2 are all *something oxide*.

These four types of oxides fit into the above three categories as follows:

Basic	Amphoteric	Acidic
R_2O	R_2O_3	RO_2
RO		

Note the R:O ratio in these four types:

2:1	⅔:1	½:1
1:1		

Proportion of oxygen increasing from left to right.

So we have learned already how just looking at the chemical formula of an oxide will tell us something of its nature. For example, K_2O (category R_2O) will be a flux, SiO_2 (category RO_2) will be glass former, and B_2O_3 (boric oxide — category R_2O_3) will be intermediate in properties and can act as both a glass former and a flux. There are some oxides that do not fit into this simple model too well (e.g. colouring oxides and opacifiers), but it is quite adequate for what we want to do.

Note: The term RO is also frequently used to mean the sum total of all the fluxes, including those in the form 'R_2O'.

GLAZE – A GLASSY MIX OF OXIDES

The relationship between Recipe, Oxide Weight % and Seger Formula.

It is possible to make very simple glazes by mixing lime, alumina and silica in the right proportions and firing to the appropriate temperature. The lime is the flux, the alumina is the stiffener, and the silica is the glass former. The melting point of any mix varies according to the proportions of the ingredients, most mixes in the lime-alumina-silica system melting well above stoneware temperatures.

There is, however, a well known eutectic (this will be explained more fully in Chapter 13) that melts at 1170°C. Table 2.3 shows the composition of this eutectic expressed in 3 ways. See table 2.3.

Wherever possible in this book I have expressed glazes in these three forms:

- The *recipe* is the list of ingredients mixed together before the firing to produce the oxides after the firing in the proportions indicated. The recipe is a weight figure and is usually expressed as a percentage.
- If you could weigh the various oxides present after the firing and express the amounts as percentages, this would give you the *oxide weight % figure*.
- If you could count the number of molecules of the various oxides and express the results as a ratio (so many of this oxide to so many of that oxide etc.), this ratio gives a *molecular formula*. If this ratio is mathematically adjusted so that all the fluxes add up to 1.0 exactly, this is a *Seger formula* (or Seger ratio or Unity formula). (In this case there is only one flux, CaO.)

I will now illustrate how both the recipe and the oxide weight % figures can be derived from the Seger formula; instead of using the example above, I will use the case of pure anorthite because it is dealing with whole numbers and is, therefore, easier to illustrate. Anorthite (lime feldspar) melts to form a glaze at 1550°C (2822°F) and has the molecular formula, $CaO.Al_2O_3.2SiO_2$. This means: one molecule of CaO to one molecule of Al_2O_3, to two molecules of SiO_2. But what is the oxide weight % figure corresponding to this formula, and what is a recipe that will give this formula when fired?

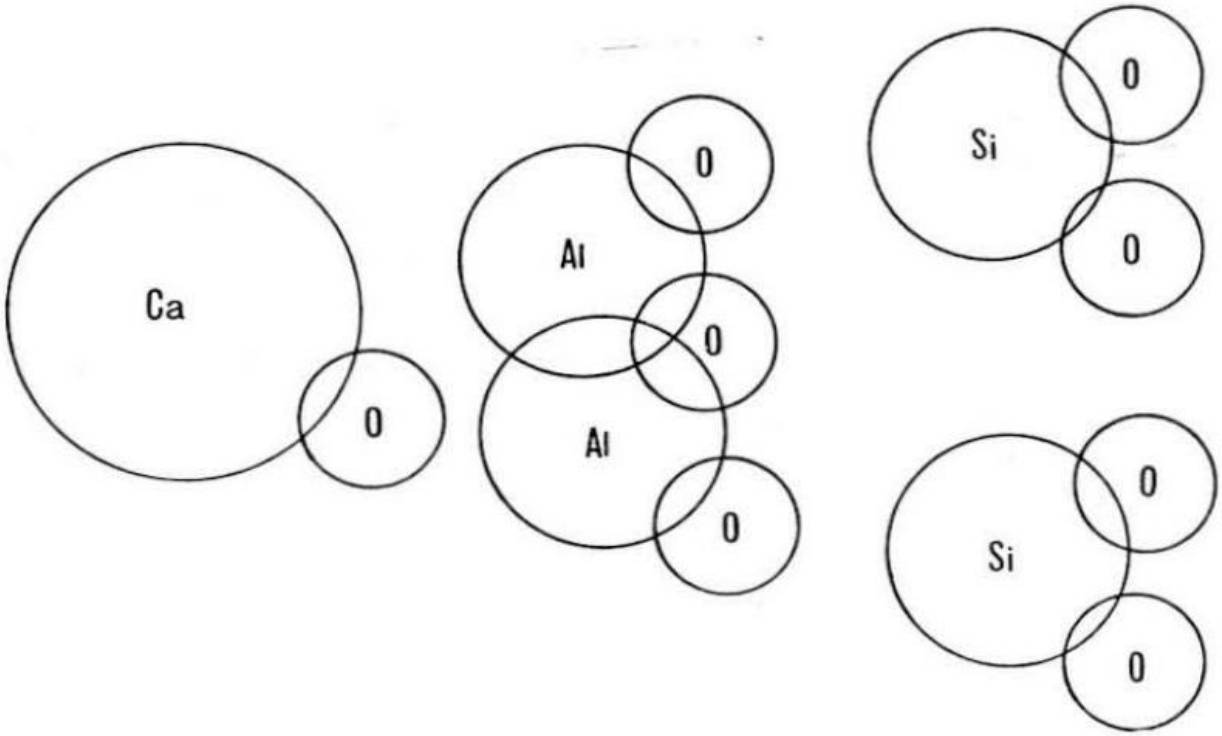
TABLE 2.3 — CaO-Al_2O_3-SiO_2 Eutectic, MP 1170°C

Ingredients before Firing		Oxides present after firing		
Typical Recipe			OXIDE	SEGER
INGREDIENTS	WEIGHT %	OXIDE	WEIGHT %	FORMULA (Molecular Parts)
WHITING	33.9	CaO	23.3	1.0
KAOLIN	30.6	Al_2O_3	14.7	0.35
SILICA	35.6	SiO_2	62.2	2.49

CONVERTING A SEGER FORMULA TO OXIDE WEIGHT %

Let us look closely at the Seger formula or molecular formula for anorthite, this time drawing out an imaginary representation of the atoms (who knows what they really 'look' like?) symbolising each atom with a circle with a diameter roughly proportional to its atomic weight. Thus, anorthite ($CaO.Al_2O_3.2SiO_2$) can be represented as follows:

DIAGRAM 2.1



Molecular Proportion	:	1 of CaO	:	1 of Al_2O_3	:	2 of SiO_2
Molecular Weights	:	56.1	:	101.9	:	(2 of) 60.1
Weight Proportion	:	56.1	:	101.9	:	120.2

These proportions of the three oxides represent an oxide weight figure that can be converted to a percentage by a simple mathematical technique, explained in Chapter 14, to give the following figures:

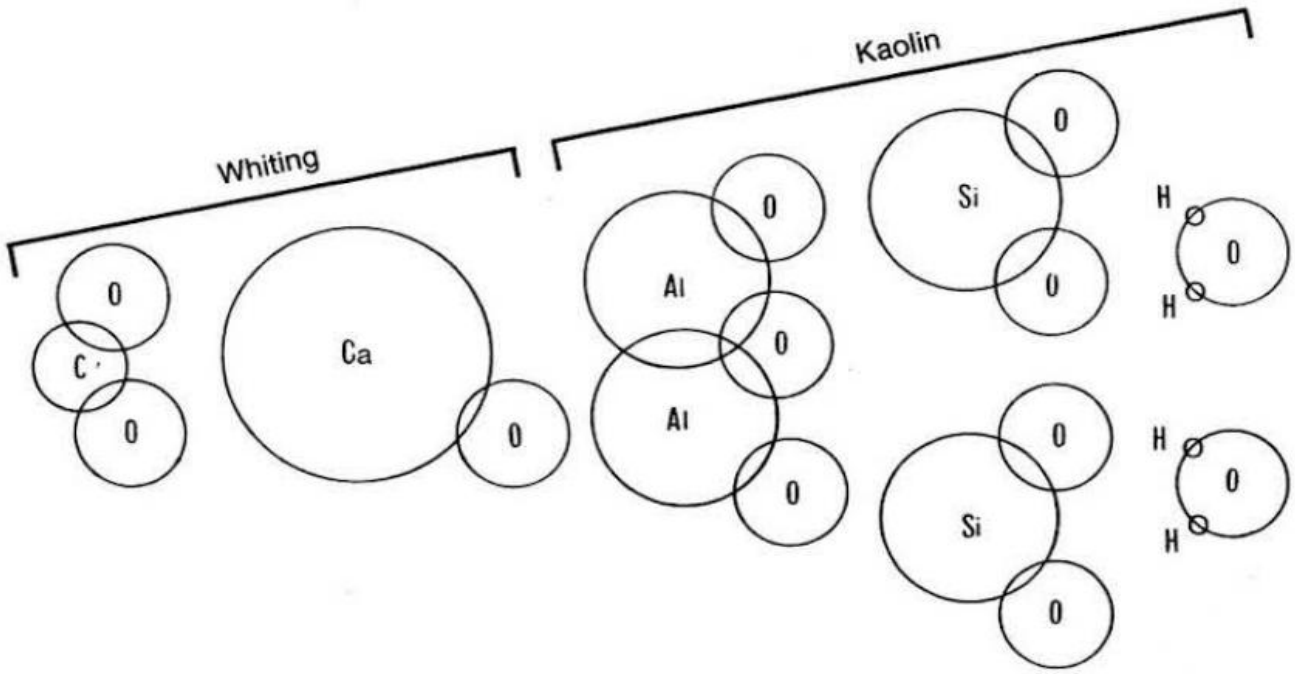
Oxide Weight %	:	20.2% CaO	:	36.6% Al_2O_3	:	43.2% SiO_2

If it were not for the inconvenient behaviour in water of some of the pure oxides, these figures could actually be used as a recipe — they are after all weight figures; however, we normally choose more convenient ingredients than the pure oxides to make up our glazes, so I will now show how to convert from formula to a normal recipe.

CONVERTING A SEGER FORMULA TO A RECIPE

Note that the basic calculation is exactly the same as for the previous example; we multiply molecular proportions by molecular weights to give weight proportions. Let us use anorthite again as our example, using whiting as the source of CaO, and kaolin as the source of Al_2O_3. To make the problem easier to follow, we will write $CaCO_3$ thus — $CO_2.CaO$ (we have simply juggled the atoms around). By studying the following diagram, you will see how theoretically you get the same fired result as before using one molecule of whiting to one molecule of kaolin:

DIAGRAM 2.2



Before firing: 1 molecule of whiting + 1 molecule of kaolin

$CO_2.CaO$ + $Al_2O_3.2SiO_2.2H_2O$

After firing:

1 molecule of carbon dioxide	1 molecule of anorthite	2 molecules of water

The carbon dioxide and water burn off leaving the desired 'glaze' that would be an artificial anorthite if the required temperature were reached.

Now using the same format as before to get the recipe:

Molecular Proportions	:-	1 of whiting	:	1 of kaolin
Molecular Weights	:-	100	:	259
Therefore Weight Proportion	:-	100	:	259

Converting these figures to percentages:

RECIPE %	:-	27.9% whiting:	72.1% kaolin

Note that if the molecular formula had demanded more silica, we would have been able to add it as free silica. If, however, we had wanted *less* than 2 molecular parts of silica, we would not have been able to use kaolin exclusively as our source of alumina because as soon as we satisfied the requirement of alumina (1 molecular part), we immediately have too much silica.

The term *molecular parts*, or abbreviated to *M.P.*, is used simply because one is usually dealing with 'parts' of a molecule rather than full molecules as we did in the anorthite example. You can usually substitute the word *molecules* without loss of meaning. Thus, *0.2 M.P. CaO* means the same as *0.2 molecules of CaO.*

If you wish to follow this through at this stage to see how to do a standard conversion to calculate a recipe from a formula for a normal stoneware glaze, see 'Using a Conversion Chart' in Chapter 14, 'Calculations'.

3 GETTING STARTED— MATERIAL REQUIREMENTS

GLAZE MATERIALS

To give you some idea how much of the various materials you will need, I will indicate what I think is necessary for a group of ten people. For the base glazes experiments, you will probably find that 100 mL of one glaze will provide enough for ten people and still not be scraping the bottom, so to speak. So I will base all my quantity calculations on providing at least 100 mL of each test glaze (with the exception of Experiment 1 on Ash/Rock/Clay Glazes).

You may find, even if you are working alone, that you prefer to make up your test glazes in this quantity. Certainly if you try to make the quantities too small, inaccuracies are bound to creep in, and it is no more trouble to make up glazes in 100 mL lots than in 10 mL lots. However, you may want to save a few dollars on materials. If so, it is a simple matter to, say, divide all my figures by 2 to get 50 mL samples. In the base glaze experiments there are 35 glazes in each set, and these are made by blending the four 'corner' glazes corresponding to the four corners of the alumina/silica graph. If you weigh out 600 grams of each corner glaze, this is adequate to produce 100 mL of each individual glaze.

So, assuming you will make up 100 mL of each test glaze, the following quantities should be adequate:

Potash Feldspar	10 kg
Whiting	5 kg
Kaolin	10 kg
Silica	10 kg
Light Magnesium Carbonate	500 grams
Barium Carbonate	2 kg
Zinc Oxide	500 grams
Lithium Carbonate	500 grams

Plus small quantities of the following colouring oxides and opacifiers:

cobalt oxide
copper oxide
iron oxide
chrome oxide
maganese oxide
nickel oxide
titanium oxide and/or rutile
tin oxide
bone ash
zircon

Notes:

1. See 'Guidelines for Selection of Materials' in Chapter 1 for details of acceptable and unacceptable materials.

2. Set aside enough materials to do the whole series of tests — and perhaps more, if you think you may wish to go beyond the 8 sets of glazes examined in detail here. This avoids the possibility of introducing extraneous variables if, for example, a new batch of feldspar is introduced half way through the series.

3. Barium carbonate is *poisonous* and should be treated with respect.

4. Avoid breathing in dust from ceramic materials; many are dangerous.

CLAY MATERIALS

You will need clay for 'individual tiles', for 'assessment tiles' and kiln setting clay:

Note: The first job to be done is making and bisque firing the assessment tiles and individual tiles. Get this done as soon as possible because very little can be done until it is.

1. Individual Tiles - Bisque Fired

The individual tiles should be made of fine white stoneware or a porcelain clay. Even if you normally do not use such clays, you will learn much more by using them because they interfere less with the variables we want to study than would a darker body.

Make at least 100 per person, preferably 200. After rolling or cutting slabs about 5 mm thick, cut the tiles 50 mm square, and make an impression in one corner as shown in Diagram 3.1:

2. Assessment Tiles - Bisque Fired

I usually do 3 or 4 large assessment tiles for each set of glazes and also a number of small assessment tiles (about half-area), which are often just a flat piece of clay, and which I tend to use for preliminary firings, special firings and draw trials. I suggest at least 3 large assessment tiles, plus 3 to 6 smaller ones, for each set of glazes to be done. The large walled assessment tiles (see diagram) are easiest made by pressing and rolling a slab of clay onto a plaster mould. The mould is made by taking a flat rectangle of plaster, 115 mm by 150 mm, and cutting into it to a depth of about 3 mm, the border, walls and central support. The walls contain the glazes during application and firing; the border provides a bearing surface for the kiln wadding to separate the tiles when fired in stacks, and the central support prevents the tile sagging in the middle in high firings.

3. Kiln Setting Clay (Kiln Wadding)

This is just a very refractory clay which is still soft and porous after a stoneware firing. I use the same mix for supporting cones, between kiln shelf and props, supporting test tiles, putting dobs under pots with runny glazes etc.

I use a plastic kaolin with lots of sand mixed in. Alternatively you could make some by mixing equal volumes of silica and kaolin and adding enough ball clay to hold it together. The mixture should hold together before the firing but be easy to remove after.

DIAGRAM 3.1 Individual Tile

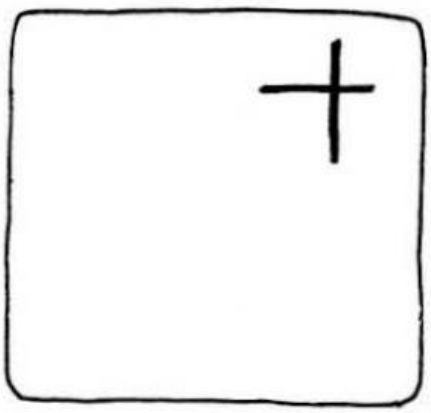
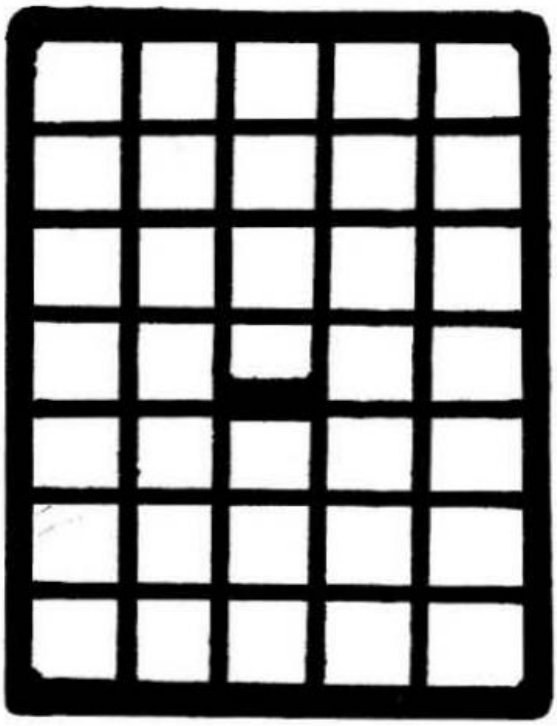


DIAGRAM 3.2 Assessment Tile



The borders marked in black are raised about 3mm. above the rest.

EQUIPMENT AND BOOKS

1. Scales

If you can afford them, the Ohaus Triple Beam Balance with Tare Poise is one of the best (the tare poise allows you to put an empty bucket on the pan and adjust the reading to zero).

Also the Ohaus School Balance is adequate and a lot cheaper, though not quite as useful in the pottery.

You need to measure to about one-tenth of a gram accuracy, and up to at least 100 grams, preferably 600 total capacity.

Get your scales tested by putting on standard weights, perhaps at the local Post Office or any local scientific or educational institution that has a set of accurate weights to calibrate your scales.

2. Sieve and Bucket

You will need a fairly fine sieve -- at least 80 mesh. You could buy a piece of 80 mesh sieve wire from your pottery supplier — about 200 mm square should be plenty — and make one as explained below. You also need a small plastic basin (or collander or bucket) that you can cut the bottom out of (this takes the sieve wire) and a bucket with a top diameter such that the sieve sits neatly inside.

If you do not have an 80 mesh sieve, you can make one up as follows:

Purchase some of the mesh from your pottery supplier and a plastic basin from the hardware store (or a small bucket or colander). The bottom of the plastic basin should be smaller than the piece of mesh. Cut the bottom out of the plastic basin, and cut the mesh 1/4" larger all round (Diagram 3.3). Carefully trim the cut edges of the plastic and mesh, because it would not be possible to do so after joining. To master the joining technique, practise first on the offcuts of plastic and mesh. You simply warm up a soldering iron or suitably shaped piece of steel, and apply it to the mesh with the plastic underneath. When the plastic melts through, the join is made. When you are satisfied with your technique, place the circle of mesh on the upturned basin and tack it in place (four spots) pulling the mesh tight as you do so (Diagram 3.4). Keeping the mesh tight, run the iron slowly around to fuse the plastic to the mesh along the full circumference. (Diagram 3.5)

Once the glazes are weighed out and water added, they will be thoroughly mixed by passing through this sieve. It is more convenient if the sieve will sit neatly in the top of a plastic bucket during the sieving operation, so try to choose your plastic implements accordingly.

3. Brushes

A small soft paint brush (e.g. 2 cm) will be needed to coax materials through the sieve; also a fine artist's brush for painting on oxides.

4. Paper Cups

For the entire course on base glazes, you will require 290 paper cups. I suggest at least 150 mL volume, preferably with a wide base, so they do not tip over easily and you can fit your test tiles in easily when applying the glaze.

5. Cartons

A few cut down cardboard cartons will be useful for storing sets of glazes; and if you are going to apply the glazes at one place and transport the tiles to another for firing, you will definitely need a shallow container of some sort.

6. Spirit Pen

This is used mainly for marking the paper cups.

DIAGRAM 3.3

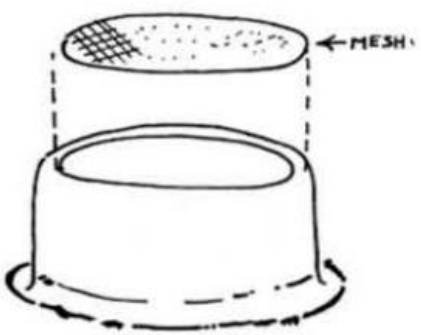


DIAGRAM 3.4

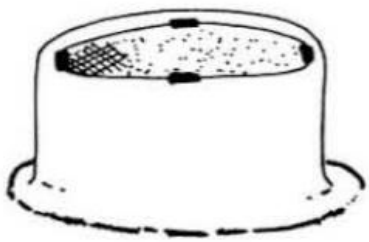
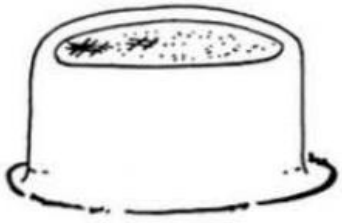


DIAGRAM 3.5



7. Graduate Syringe (Plastic)

This will be used for measuring out the glaze in volumetric blending. The size depends on the size batches you are going to make up. I suggest you get small (10 mL) and large (around 50 mL) ones. You may find it is useful to have two or even more for your group since it is possible for more than one person to be measuring out on the same experiment at the same time, considerably speeding up the process.

They are obtainable from veterinary surgeons and doctors' surgeries. They regularly need lubricating; use vaseline.

8. Measuring Cylinder or Measuring Jug

I think most groups will need about a one litre measuring cylinder. A plastic scientific measuring cylinder is ideal (plastic is cheaper and more robust than glass), but you may be able to buy locally a tall narrow transparent graduated measuring jug! The narrower it is, the more accurate your measurements will be. Almost any tall transparent container will do in a pinch; its purpose is to bring different glaze mixtures to exactly the same volume; you do not need to know the actual volume.

9. Plastic Buckets

Apart from the bucket that goes with the sieve, you will need at least four small plastic buckets or large ice cream containers, preferably with lids. It is a good idea to have plenty of spare containers.

10. Electronic Calculator

You need one if you intend working through the calculation techniques, and probably even if you do not. You do not need anything fancy -- just add, subtract, multiply and divide is all you really require. However, if you are willing to teach yourself how to use them, the following functions are useful on your calculator:

(a) memory
(b) % key
(c) constant (K) key;

this last one is usually incorporated in the '=' key and allows you to multiply or divide a long list of numbers by a constant number to give the long list of answers with a minimum of work on the keyboard.

11. Books

Students doing the Australian Flying Arts School correspondence course are recommended to get *Glazes for the Craft Potter* by Harry Fraser (Pitman) as a reference for beginners (Australian price: $23.00 (1986), and if possible, Frank Hamer's *Potter's Dictionary of Materials and Techniques* (Watson-Guptill), which is recommended as an excellent general reference (Australian price: $80.00 (1986). Also see other books mentioned in the 'Introduction'. (Page 3).

12. Mortar and Pestle

These may prove useful.

13. Hand Lens

14. Journal

A large book with permanent pages, to record all calculations, details of experiments, of kiln, firing, glazes etc. Every potter has one.

15. Kiln

Almost any stoneware kiln will do, bearing in mind that different kilns will give different results. If firing in a wood-fired kiln, the base glaze exercises need to be protected from the effects of ash and vapour in initial testing by firing inside an unglazed pot or saggar.

4 LINE BLENDS— Ash, Clay and Rock Glazes

Natural glazes are discussed in some detail in Chapters 25 and 26 but ash, clay and rock glazes are introduced here to illustrate the process of line blends and volumetric blending and to give some balance to the rest of Part I where we deal as far as possible with theoretically 'pure' materials.

To illustrate the method of doing line blends, we are going to investigate some traditional glazes with pedigrees going back thousands of years. In China the first glazes were natural ash glazes, resulting from the melting of fly ash that landed on the pots during the firing. Later they took to adding clay to the ash and applying it to the pots, and later still, rock dust was added.

Let us start with a few hints on collecting and preparing ash, rock dust, and clay for use as glaze ingredients.

WOOD ASH

Collection

About the easiest way to collect ash is to burn it yourself in a wood stove. This way you will know the type of wood and can keep it free of sand etc., and no special effort is involved.

Note: For the few days in which you are collecting the ash, do not burn rubbish in your stove. If you do not have access to a wood stove, any wood ash will do. The main advantage in burning your own is that you have a greater chance of repeating your results – ashes are enormously variable in composition. If the ash is properly burned, it should be white or grey or buff, without too much charcoal.

For this experiments, we want the ash to act as a flux, so do not use grass ashes, as these are usually low in fluxes and high in silica. However, you will find that grass ashes have special application elsewhere.

Note: Bamboo, sugar cane, rice, wheat etc. are all grasses.

Preparation

There are a number of ways to get the ash ready for use as a glaze ingredient. It can be used either washed or unwashed.

Unwashed ash — This is the simplest way to prepare your ash. It is dry sieved through a coarse mesh (e.g. insect screen) to remove charcoal, stones etc., and this ash is weighed out into the glaze batch, which is then sieved through an 80 mesh sieve, or ball milled, to produce a fine particle size. In other words, there is virtually no preparation done to the ash until it has been mixed with the rest of the glaze. In this way the soluble fluxes are retained and are present in the water of the glaze batch. The results will usually be different from the washed ash method.

Washed ash — Add plenty of water to the ash and stir it up. The charcoal should float and is easily scooped off the surface with a coarse sieve. If you then pour off the ash and water, you should leave behind any sand and gravel, which settles out quickly. The ash is then coaxed through an 80 mesh sieve, allowed to stand for 24 hours, and the water is decanted off. More water is added, and the process repeated several times. According to Bernard Leach, it should be repeated until the water is 'clear and tasteless'. However, the number of washings is entirely up to you, depending on how much, if any, of the soluble fluxes you want removed. It should then be dried and is ready for use as a glaze ingredient.

See *Glazes for the Craft Potter,* page 35, for a simple summary on preparing wood ash by washing. For a more thorough treatment of wood ash and vegetable ash, see *A Potter's Book* by Bernard Leach, pages 159-164. You probably already have Leach's book or have access to it. It deserves a place on every potter's bookshelf, being the first textbook in the

west to reveal the secrets of stoneware pottery, and after forty years of publication still one of the most useful books available, especially if your tendency is towards the use of natural materials and wood firing.

CLAY

I suggest you use a local clay in these glazes since it will probably be more interesting than using bagged ball clay, China clay etc.

Many red clays will produce a glaze at stoneware temperature with little or no additional fluxes and give interesting results.

The clay may not need any preparation if it is reasonably free of grit and vegetation. Otherwise, you should slake it with plenty of water, sieve it (80 mesh), let it stand, decant off excess water and dry the product. Some clays do not slake easily, or at all, and need to be pulverised by some means (see the section on rock dust).

ROCK DUST

You can collect rock dust from the local crusher where they make the 'blue metal' for bitumen roads. Very fine dust will collect in nooks and crannies around the crusher building on horizontal beams etc. and is usually fine enough to be used as is, in your glazes.

If you have a particular type of rock you want to use in glazes, you will have to pulverise it by some means. If there is a mining or geological laboratory near you, they might be willing to break it up for you. It is a simple matter for them to put it through a small jaw crusher which usually breaks it down to about gravel size, and it may be easy for them to take it down to glaze size (100 to 200 mesh), or you might be able to grind the 'gravel' in your own ball mill (see later). Alternatively, you can dolly your rocks using a heavy mortar and pestle. The mortar is made up from a half metre length of steel pipe with one end sealed off, and for the pestle you could use the flat knob end of a crow bar. This sounds like very heavy work, but a lot of rocks will break up easily if you first bisque fire them. Also see Cardew, page 215, on the use of an ordinary corn mill to reduce small pebble-sized rocks to a fine sand and even finer. Once you have it down to a pea-size gravel, you can leave the rest of the work to the ball mill; and if you cannot afford to buy one, and would like one, read on.

BALL MILLS

The real thing costs a lot of money, and if you want the latest sort of vibro-energy mill such as the Op-po (see Fraser, pages 79-81), you will part with a staggering amount of pots to pay for it. However, it produces superfine material in minutes instead of hours or days by the conventional ball milling method. But for those of you who do not have money to burn and if you do not mind waiting half a day or so for the results, I submit the following suggestions for making an old-fashioned mill yourself.

You may be able to obtain or borrow a gem tumbler and use home-made porcelain balls that have been fired as high as you can manage in your kiln. Some people use a beer fermenting barrel instead of the traditional porcelain mill, for about a twentieth of the price. If you want to make your own mill, balls and rollers, read Michael Cardew's book, *Pioneer Pottery* (published by Longman), pages 275-285, for all the relevant information. This book ranks next to Leach's *A Potter's Book* in importance and relevance to potters working with natural materials and especially for people in isolated situations.

Also see *Thoroughly Modern Milling* by Stephen Harrison, published by The Potters' Society of Australia and available through them or from pottery suppliers.

VOLUMETRIC BLENDING - LOTS OF GLAZES WITH LITTLE WORK

Experiment No.1
Volumetric Line Blend of Wood Ash with Rock Dust or Clay

We want to use the ash in varying proportions with a clay or rock dust. Even if the clay or rock will not melt of its own accord, by progressively increasing the amounts of ash, we should find a proportion at which the ash will flux the other material to produce a glaze. A neat way to do this would be to prepare the eleven glazes illustrated in Table 4.1.

We now have eleven glaze recipes, each recipe adding up to one hundred parts by weight. It would be a lot of work to weigh out, wet up and sieve each of the eleven glazes individually, however. With a line blend, where the glazes are a steady progression between two extremes (say, 100% ash to 100% rock dust), we can obtain all the intermediate glazes just by mixing together the two 'end' glazes in the correct proportions.

TABLE 4.1

Glaze No.	0	1	2	3	4	5	6	7	8	9	10
Ash%	0	10	20	30	40	50	60	70	80	90	100
Rock Dust or Clay%	100	90	80	70	60	50	40	30	20	10	0

For example, if you mixed equal parts by dry weight of glaze 0 and glaze 10, the resultant mix would have a composition halfway between the two, i.e. glaze no.5. But usually the two end glazes will be wet, not dry, by the time you have them uniformly mixed and ready for mixing together.

Note: This does not really apply here where the two end glazes contain only one ingredient each; but usually the two end glazes will have several ingredients, which are mixed by wetting and sieving.

How do we mix 'equal parts by dry weight' with glazes that are not dry? The answer is to make sure that the two end glazes have the same dry weight in the same wet volume. Then in order to get glaze no.5., we can mix equal parts by *volume,* and know that this will also give us equal parts by weight. To explain further, here is an example showing how to get glaze no.5 by volumetric blending of the two end glazes:

First weigh out 100 grams of glaze no.0 and 100 grams of glaze no.10, and make each up to the same volume, say 120 mL. If you then mix one spoonful of glaze no.0 with an equal spoonful of glaze no.10, the resultant mix will be glaze no.5.

To do the experiment systematically, I suggest you follow the procedure below. The volumes are quite small but enough to glaze several sets of small test tiles.

Experimental Procedure

1. Weigh out 100 grams of glaze 0, i.e. 100 grams or rock dust or clay.
2. Weigh out 100 grams of glaze 10, i.e. 100 grams of ash.
3. Mix each with a small amount of water and sieve carefully, making sure that all the solids get through and leaving as little as possible on the sieve and brush. Any materials that remain on the sieve should, theoretically, be ground with a mortar and pestle until they pass through.
4. Make the two glazes up to exactly the same volume with more water to give a convenient consistency for putting onto test pieces. Measure the volumes in a tall, transparent plastic or glass measuring cylinder. Each 100 grams of dry glaze should make up around 110 to 150 mL of wet glaze suspension. The actual number of mL does not matter as long as it is exactly the same for both.
5. Set out eleven paper cups with the glaze numbers marked on in spirit pen.
6. Starting with glaze 0, stir it until it is quite homogenous, and using your graduated syringe, measure out the required amounts of glaze 0 into each of the cups as shown in Table 4.2. Repeat the process with glaze 10. You now have your line blend.

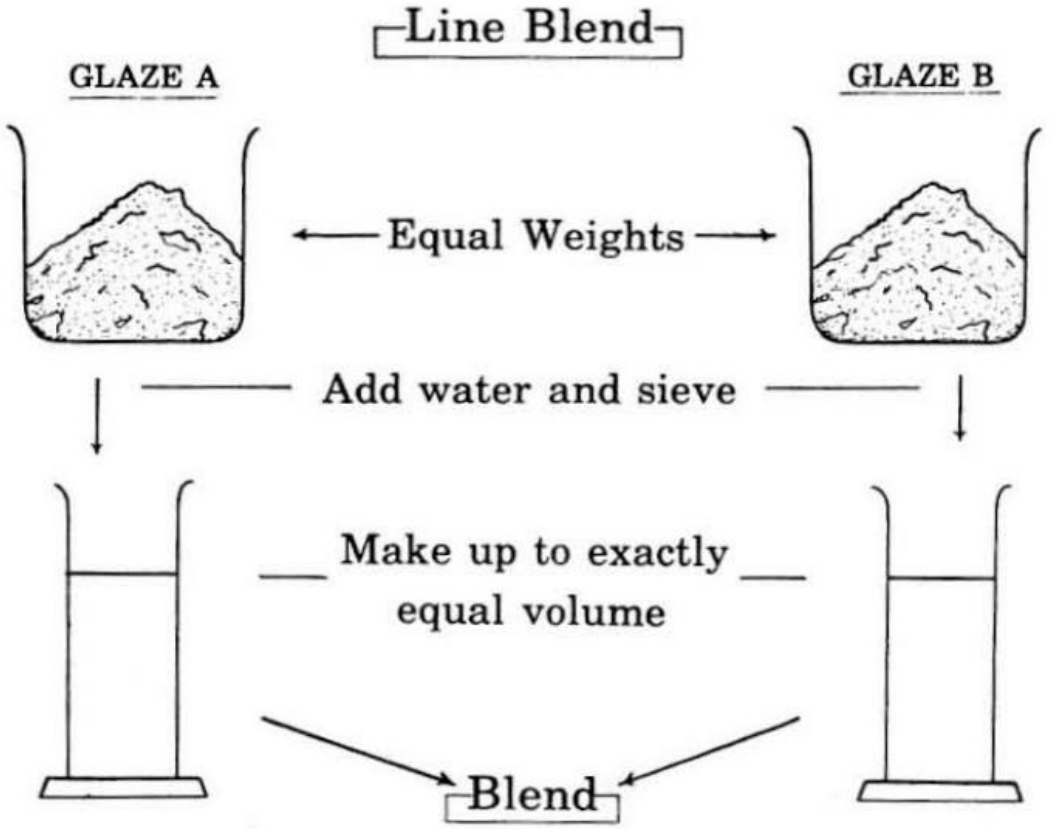
Notes:

a. It is important that the solids should be uniformly in suspension when filling the syringe (so keep the glaze well stirred) and that they should not be given any chance to settle out in the syringe. To overcome this last problem, you could either:
   (i) work fast
   (ii) suck into the syringe exactly what is required for each cup instead of doing several cups from one syringeful or
   (iii) add about 5% Ball Clay to both

TABLE 4.2 — Showing the volumes (in mL) of glaze 0 and glaze 10 in each of the intermediate blends

Glaze No.	0	1	2	3	4	5	6	7	8	9	10
Ash	0	1	2	3	4	5	6	7	8	9	10
Rock Dust or Clay	10	9	8	7	6	5	4	3	2	1	0

Volumetric Blending



The following example shows the relationship between the blending process and the recipes of the blends:

		A	Blends			B
Blend the two glazes in these proportions (by volume) to give these recipes	Parts of A	4	3	2	1	0
	Parts of B	0	1	2	3	4
	Feldspar	60	55	50	45	40
	Whiting	40	35	30	25	20
	Kaolin	0	10	20	30	40

These are the two glazes originally weighed out.

Note the simplicity of the mathematics: the equal steps in the blending process (4 parts, 3 parts, 2 etc.) resulting in equal steps in the recipes (FELDSPAR: 60, 55, 50 etc.) This is explained in detail in the text.

glaze 0 and glaze 10, and this will suspend them (and probably give a slightly different fired result).

b. *Apply the glazes in a systematic order* to assessment tiles; otherwise you have to somehow identify each individual glaze on the tile. In this case, start with Glaze No.0 and not with Glaze No.1, a common though understandable error.

7. Mix the two glazes together in each of the nine blended cups.

8. Take eleven bisque-fired individual tiles and mark the numbers on the back with iron oxide. Your test tiles should always have one or two lines impressed into the surface to get some idea of the glaze's tendency to pool in depressions.

9. Dip each of the test tiles in turn, applying the glaze in such a way that you get a variety of thicknesses on the one piece, varying from very thin up to 1 mm or 2 mm thick. Leave one end of each tile unglazed to stick into pads of clay. Apply dobs of the eleven glazes to assessment tiles to be fired horizontally (see 'Assessment Tiles' in the 'List of Glaze and Clay Materials Required').

10. Fire the set to about large Orton Cone 10 - just do your normal stoneware firing. The individual tiles should be set in a pad of kiln setting clay (see Materials List) so that they are fired vertically. This way you learn more about the runniness of each glaze. Some people prefer little bowls, rings etc. for firing test glazes. Either of these would be all right for this set of tests, but when it comes to the base-glaze tests, you will see that the tile format has much to recommend it.

Support assessment tiles on little dobs of kiln-setting clay in the firing. Otherwise, if the tile cracks and a runny glaze runs through, it will be fused permanently to the kiln shelf.

If you are working in a group, then several of you should sample and fire each set that you make up. The more variation you get between your respective firing cycles, the more you will learn about each set of glazes that you prepare. If you yourself are in the habit of using a variety of firing cycles, you could prepare several 'assessment tiles' for your own information and fire them at different times to different temperatures under oxidation and reduction etc., depending on what sort of firing you have planned. Alternatively, fire different assessment tiles in hot and cold spots in the same firing.

If you have a lot of people wanting to sample the set, you will find you can double the volumes listed in Table 4.2 without running out of glaze 0 or glaze 10.

Labelling Test Tiles and Recording Data

Attention to this step is most important because often in the excitement of opening a kiln and getting things out, vital information is lost; and, of course there is always the case of data that are so basic you are sure you will never forget them. I suggest you record data on the assumption that you have a very bad memory.

Immediately after test tiles come from the kiln, they should be permanently labelled or glued down on stiff board, and the mounting board labelled. All relevant data should be recorded so that you can obtain the details of glaze, clay and firing when needed. This is recorded in your journal and/or directly onto the mounting board. Assessment tiles are large enough so that the data can usually be glued onto the back. Students enrolled in the AFAS correspondence course on stoneware glazes attach the following information to the back of each assessment tile they forward for the tutor to see:

a. Name of Glaze Set, e.g. 'Ash/Clay/Rock Glazes'.
b. Name of person or group and address.
c. Drawing of the final shape of the cone, the number of the cone and the brand or type of cone used.
d. Firing details, especially soaking and cooling details and whether reduced or oxidised.
e. Kiln details, e.g. 'Fibre Gas Kiln' or 'Dense Brick Wood Fired Kiln' or 'Insulating Brick Wood Fired Kiln' or 'Electric Kiln' etc.
f. Clay type used in assessment tile.
g. Type of kaolin used.
h. Any other relevant details.

REFERENCES

Glazes for the Craft Potter by Harry Fraser (Pitman).
A Potter's Book by Bernard Leach (Faber & Faber).
Pioneer Pottery by Michael Cardew (Longman).
Thoroughly Modern Milling by Steven Harrison (Potters' Society of Australia).

5 BASELINE GRIDS AND BIAXIAL BLENDS

In our study of base glazes, we want to systematically vary the three ingredients of a base glaze, i.e. fluxes, alumina and silica. This will be done by studying a number of sets of glazes, each set having its fluxes constant (in M.P.) and alumina and silica varying. For example, the 0.8 Limestone Set has fluxes fixed at 0.2 K_2O + 0.8 CaO, and the alumina and silica varies over a wide range.

The limits we can usefully explore depend to some extent on the ingredients we wish to use in the glazes and, to some extent, on the temperature range we want to examine. The base glaze experiments have been designed to examine as wide a range as possible bearing in mind these two limitations. To explain this further, let us get down to basics.

BASELINE GRIDS

Starting Points:

The starting points for our experiments will always be a 'flux' of some kind, or mixture of 'fluxes', using the term in its broader sense, to include materials like feldspars, frits, wood ash, many igneous rocks, plus all the materials that are pure fluxes, like limestone (calcite or whiting), magnesium carbonate, zinc oxide etc.
In this study of base glazes, we will use only K feldspar, and the pure fluxes: calcite, magnesium carbonate, barium carbonate, zinc oxide and lithium carbonate. These materials are obtainable either very pure, or adequately so, enabling us to reliably study the effects of varying fluxes, alumina and silica without adding significant impurities, which would confuse the issue.

Sets of glazes using igneous rocks, wood ash etc. as starting points will be suggested in the second half of the course.

Baselines:

If you take any 'flux', or mixture of fluxes and add to it progressive amounts of silica, you get a line blend that I call the 'silica baseline'. Similarly, if you take the same flux or fluxes and add progressive amounts of kaolin, you get a line blend I call the 'kaolin baseline'. (See Diagram 5.1.) Note in the diagram that the kaolin baseline slopes out from the vertical axis because the kaolin is adding silica with the alumina. This diagram could apply to any pure flux; for the sake of simple example, we will assume here that the flux is calcite, which will provide CaO in the firing. In this case I have drawn the baselines to the point where the silica baseline reaches 4 M.P. SiO_2, and the kaolin baseline reaches 0.6 M.P. Al_2O_3 and 1.2 M.P. SiO_2.

Baseline Grids:

Looking at Diagram 5.2, if you draw lines parallel to the baselines as shown, you obtain the parallelogram AB,CD that spans 4 M.P. on the silica axis and 0.6 M.P. on the alumina axis. This parallelogram shows the limits of this experiment, the individual glazes being scattered in a 'grid' pattern across its area, hence the term 'baseline grid'.

In this particular case the baseline grid is inappropriate for our experiments since only a few of the 'glazes' will melt at stoneware temperatures. This will often be the case if the starting point chosen is a pure flux not containing any glass former. But if we add a little K_2O, from feldspar, the picture changes dramatically; we will use a combination of feldspar and calcite to give the starting point 'C' on the baseline grid. The example illustrated here is the '0.8 Limestone Set', one of the sets to be studied in detail in this course. See Diagram 5.3. In this set, the fluxes are

DIAGRAM 5.1
Baselines

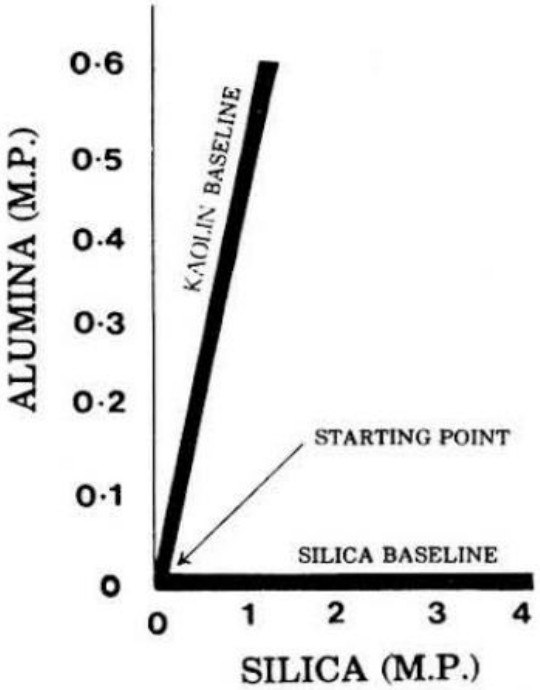
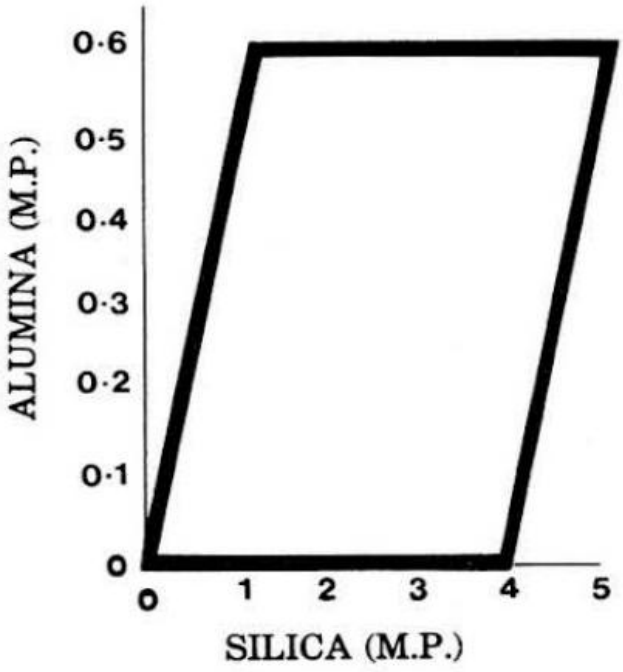


DIAGRAM 5.2
Baseline Grid



0.2 K_2O + 0.8 CaO, and the feldspar that provides the K_2O also brings in some extra alumina and silica. The whole baseline grid, is therefore, moved up and to the right on the alumina/silica chart, by comparison with the original diagram where calcite alone was used as the starting point. The array of dots on the diagram represents the 35 separate glazes that result from the technique used for mixing the glazes, 'biaxial volumetric blending'. The peculiar pattern of the dots, tending to be crowded down into Corner C, is a result of the mathematical relationship between molecular parts (as used for the framework of the diagram) and weight parts (as used in the volumetric blending technique). This pattern is probably the most useful, giving greater density of sampling where it is needed on the alumina/silica chart.

BIAXIAL BLENDS

Diagram 5.4 represents the 0.8 Limestone Set of glazes, each dot representing one glaze, 35 in all, numbered as shown. All 8 sets of glazes studied in this course contain 35 glazes arranged in this 5 x 7 layout. The glazes are always numbered in the same order. Note that for the purpose of clearer explanation the 'corner glazes' (i.e. Nos 1, 5, 31 and 35) are also referred to as A, B, C and D respectively.

Looking at Diagram 5.4, you can think of it as a series of line blends, e.g. line blend 1, 2, 3, 4, 5, (using the glaze numbers), and line blend 6, 7, 8, 9, 10, etc. So the 35 glazes consist of 7 line blends running horizontally, or alternatively you can think of it as 5 line blends running vertically. Just as it was possible in the line-blending experiment earlier (see Chapter 4) to get all eleven glazes on the line blend from one extreme to another by blending the two extremes, so it is possible to get all 35 glazes in this series by blending the *four* extremes, i.e. the 'corner glazes'. The recipes and other relevant data for these glazes are given opposite:

DIAGRAM 5.3
Baseline Grid for the 0.8 Limestone Set

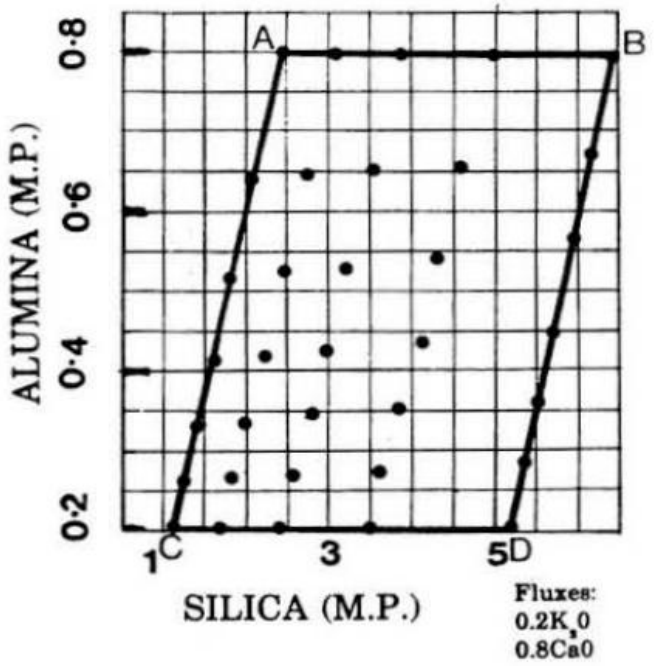


DIAGRAM 5.4
Glaze Numbers

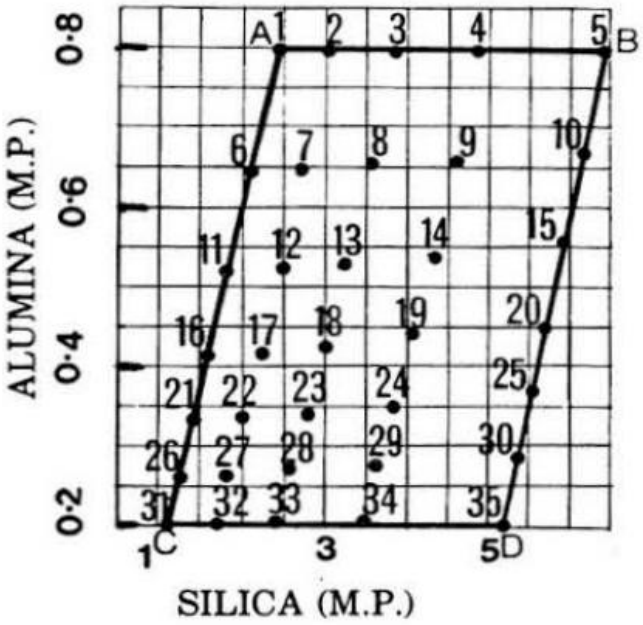


TABLE 5.1: Corner Glazes for the 0.8 Limestone Set.

	RECIPE (%)				OXIDE WT. (%)				M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	KAOLIN	SILICA	K_2O	CaO	Al_2O_3	SiO_2	FLUXES: 0.2 K_2O 0.8 CaO
									Al_2O_3/SiO_2:
A	32.15	23.13	44.73	0	6.51	15.50	28.16	49.82	0.8/2.4
B	18.97	13.65	26.40	40.98	3.56	8.47	15.38	72.59	0.8/6.4
C	58.16	41.84	0	0	12.07	28.73	13.04	46.16	0.2/1.2
D	25.78	18.55	0	55.68	4.75	11.32	5.14	78.79	0.2/5.2

6 EXPERIMENTAL PROCEDURE FOR BIAXIAL BLENDS

The aim is to prepare 35 glazes by blending the corner glazes as outlined at the end of the previous chapter (see 'Biaxial Blends') and to apply the glazes to test tiles and to fire them so as to learn as much as possible about the effect of varying fluxes alumina and silica for a chosen set of fluxes.

A. MAKING THE GLAZES

Note: As outlined under 'Glaze Materials' in Chapter 3, I will quote figures for a group of about ten people. If you wish to increase or decrease the amounts, that is up to you, bearing in mind the possibility of introducing inaccuracies if the quantities are too small. (Use at least 300 grams for each corner glaze.)

1. Weigh out 600 grams each of the four 'corner glaze' recipes, such as those given in Table 5.1. (Multiply each % number by 6 and call it grams.) See 'Guidelines for Selection of Materials', P. 8.
2. Starting with Glaze A, mix with a small amount of water and sieve carefully (80 mesh or finer) making sure that all the solids get through and leaving as little as possible on the sieve and brush. Any materials remaining on the sieve should be ground with mortar and pestle until they will pass through. Use as little water as possible and when the mixing and sieving is completed, add (if necessary) a little water, just enough to make the consistency suitable for measuring with the graduated syringe (see 'List of Equipment Required').
3. Prepare Glazes B, C and D in similar manner and add water to bring them up to *exactly the same volume* as A*. When this is done, you will notice that Glazes C and D are relatively watery because of the lack of clay in them. It was for this reason that I recommended in (2) that you make Glaze A to a reasonably thick consistency. Otherwise Glazes C and D would be so watery (by the time they were made up to the same volume as A) that they would cause problems in the syringe measuring. You need at least 900 mL of each corner glaze if you wish to use the figures I have given in the 'Parts Chart' following.
4. Set out 35 paper cups with the glaze numbers marked on in spirit pen.
5. Starting with Glaze A, stir it until it is quite homogenous and, using your graduated syringe, measure out the required amounts of A into each of the cups as shown in Diagram 6.1, which I call a 'Parts Chart'. Repeat the process with Glazes B, C and D. See Diagram 6.1 following. (*Note:* Avoid getting air bubbles in the syringe and avoid the solids settling out.)
6. Stir the blends in each of the 35 cups. You now have your 35 glazes. This whole process, from (1) to (5) should take one person, working alone, about three hours.

B. APPLYING THE GLAZES AND OXIDES AND FIRING

The glazes are applied to two types of test tiles:

1. assessment tiles, where all 35 glazes in the set are applied in their 5 x 7 pattern on one tile, about 150 x 100 mm overall dimensions, and
2. individual test tiles, where one glaze only is applied to a tile about 50 mm square, usually with colouring oxides brushed on.

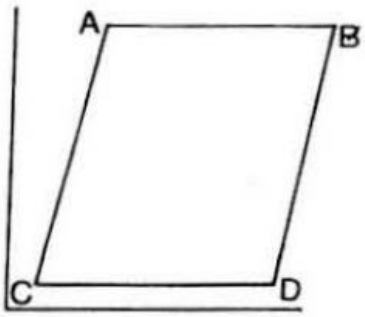
The idea is that one fires assessment tiles first under different conditions to get an overall view of the glaze phenomena

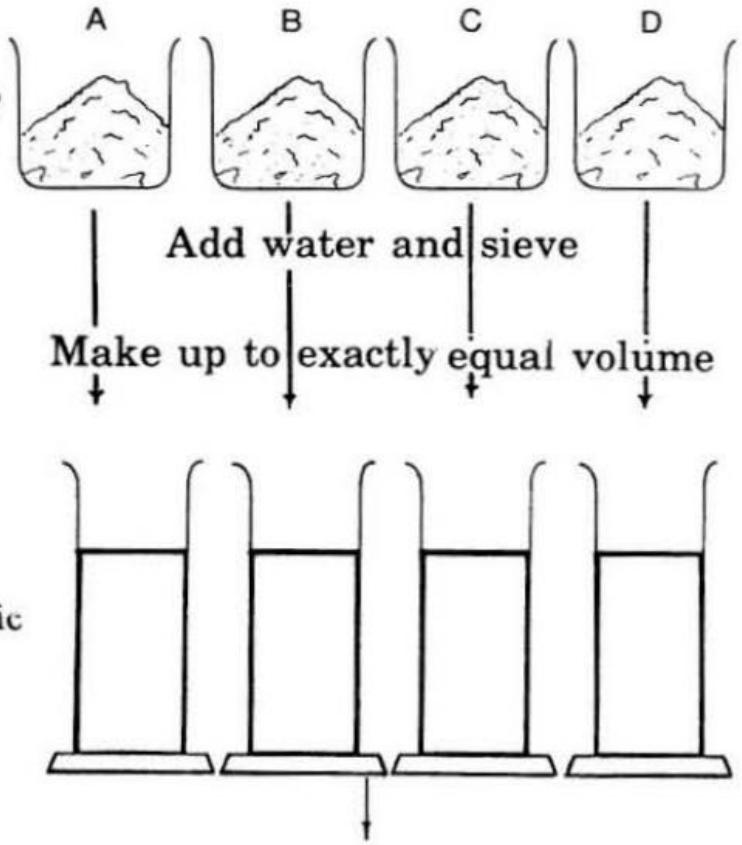
* Note: Some authors suggest equalizing the four corner glazes by *weighing* the cylinders of glaze and adding water until the weights are equal. This is incorrect, however, *unless the blending process is also done by weighing.* In our case, the blending is *volumetric,* so the equalization process *must also be volumetric.*

Volumetric Blending - Biaxial Blends

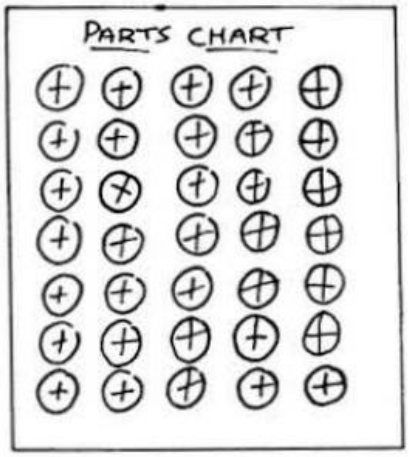
Equal Weights

Recipes for ABC & D (the corner glazes) are given in the text.



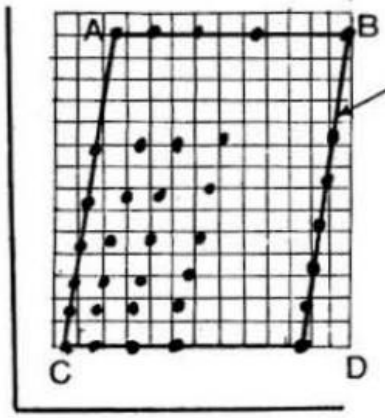


Blend according to volumetric proportions indicated in the Parts Chart.



Blend
to give 35 glazes

The 35 glazes are represented by the dots on the alumina silica chart.

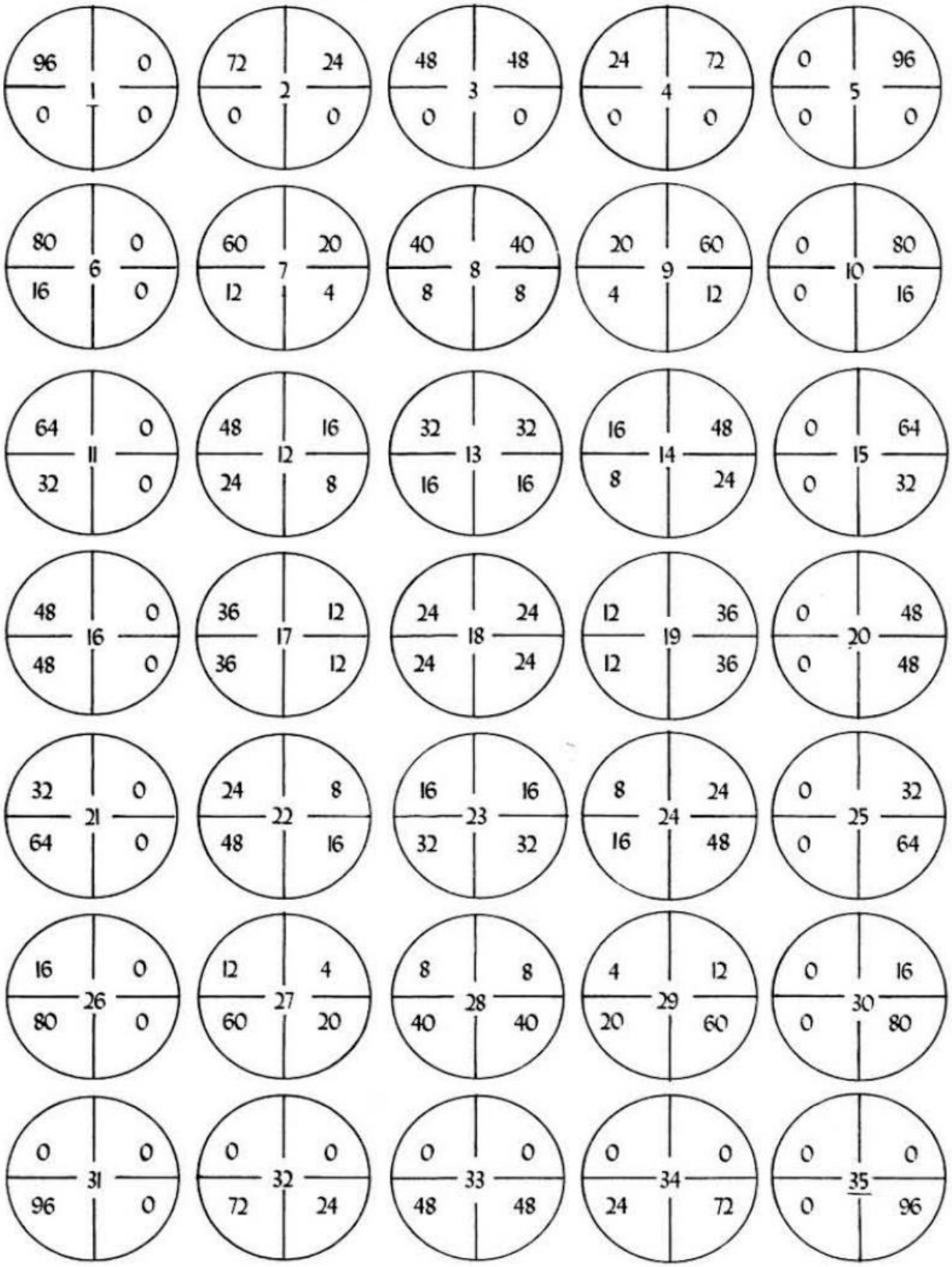


The recipes and other data for all 35 glazes are presented in the data sheets.

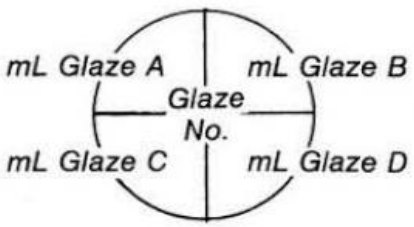
DATA SHEET

GLAZE N°	RECIPES	Oxide Wt %	M.P.
1			
2			
3			
⋮			
35.			

DIAGRAM 6.1 - Parts Chart
Volumes in mL of each of the four corner glazes to make up Glazes 1 to 35



Key:



Notes:

1) The 35 glazes above are set out in the same order as in Diagram 5.4.
2) Using these figures, you will get 96 mL of each glaze, which is adequate for at least 10 people.
3) If you have decided to use less than the recommended 600 grams for each corner glaze, the Parts Chart must be adjusted accordingly, e.g. if using 300 grams of each, divide all the mL figures in the Parts Chart by 2.

that occur on the different glazes and in different firing conditions, and to give an idea which glazes warrant closer inspection and the best firing conditions for them. A fair amount of work goes into preparing and firing the individual tiles, so you do not want to ruin them; also, in some areas, you will find you will be satisfied with individual tile samples of perhaps every second glaze.

Assessment Tiles

When I go to as much trouble as this to prepare a set of glazes, I like to get as much out of it as I can. I would usually prepare about ten assessment tiles, including a couple of dark clay. It takes relatively little time if you apply the glazes with a syringe. I usually fire three or four in the first firing and the rest in future firings. Used like this, the assessment tile can become an excellent tool in glaze research. If an unusual firing is being done, and the potter wishes to learn as much as possible, it is a simple matter to include a range of assessment tiles taken from careful storage, having been prepared months or even years before at the expense of a few extra minutes' work.

Take at least 6 assessment tiles, all made from fine white stoneware or porcelain clay. If you wish to try darker stoneware clays, this should be in addition to the tiles just mentioned. Coloured clays or coarse clays will often mask the effects we want to observe, though they may provide interesting results.

Note: As you apply the glazes to the tiles, you will find that you need to adjust the amount of water in the individual containers to get the right consistency. Usually you will have to add water to the top rows of glazes, and decant excess water from the bottom rows. Keep the glazes agitated while sampling, to prevent heavier materials from setting out.

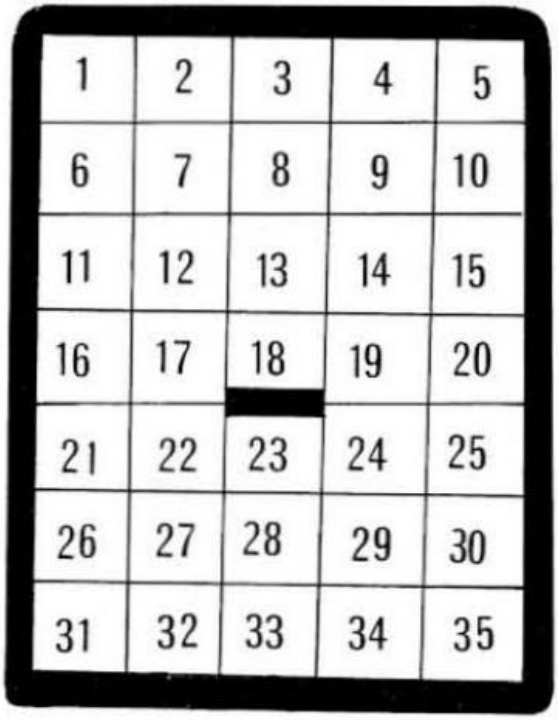
Apply a thick dob (2 mm thick) of each glaze in the positions indicated by the numbers on Diagram 6.2. There is no real need to number the glazes on the assessment tile as long as one corner is somehow marked. The assessment tiles are not really large enough for general application of colouring oxides, but some useful information can be gained if you work carefully. I suggest you apply no more than 1 or 2 colourants per glaze, that they be applied as a spot about 1-2 mm across, and that every second glaze is usually adequate coverage for any one oxide.

Firing Assessment Tiles

After preparing the first set of glazes, say, the 0.8 Limestone Set, I recommend firing 1 or 2 assessment tiles just to check that things are not dreadfully amiss. You need to be confident that your raw materials are right, particularly those used in all the sets, and also that your experimental procedure is adequate before investing many hours work in producing up to 8 different sets of glazes. The initial results can be compared with the Results Charts given later.

The assessment tiles are normally meant to be fired in stacks, one tile from each set, so one can make comparisons between the different sets fired under virtually identical conditions. The tiles are fired horizontally, separated from each other and from the kiln shelf by dobs of kiln wadding. This enables the tiles to be separated easily after the firing, if tiles crack and runny glazes run through, and also allows free passage of the kiln atmosphere between the stacked assessment tiles. I usually put a blank tile as a 'lid' over the top one. Pyrometric

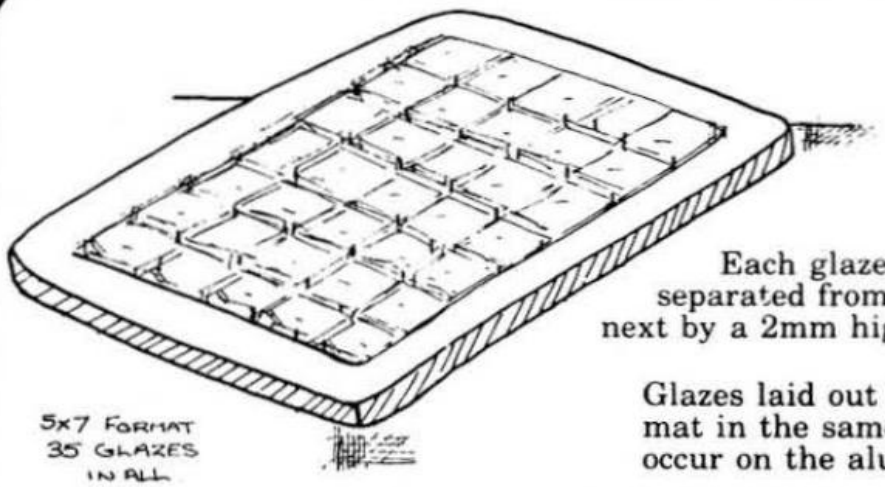
DIAGRAM 6.2 - Assessment Tile



Note: Print the name of the set in iron oxide on the *edge* rather than on the back, lest the iron affect the glazes underneath when tiles are fired in stacks.

Assessment Tiles

for preliminary testing

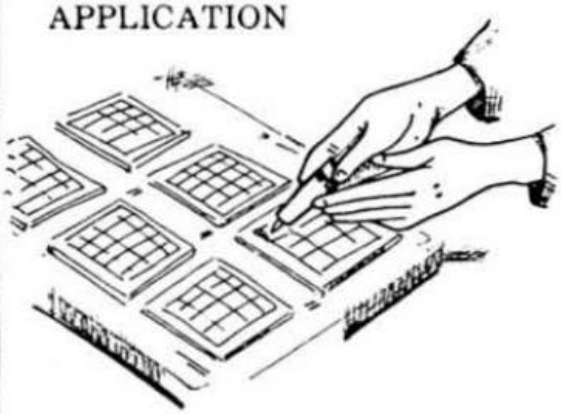


Each glaze separated from the next by a 2mm high wall.

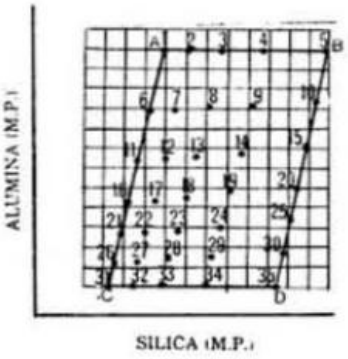
Glazes laid out in the 5x7 format in the same order as they occur on the alumina/silica chart.

1	2	3	4	5
6	7	8	9	10
11	12	13	14	15
16	etc	'	'	'
'	'	'	'	'
'	'	'	'	'
'	'	'	'	'

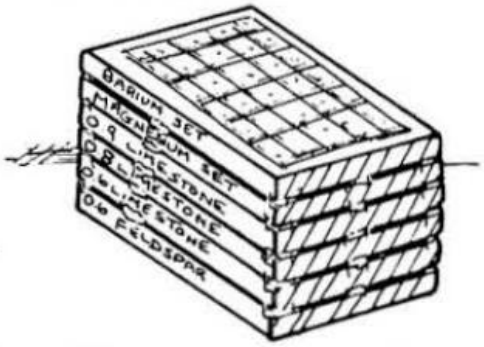
APPLICATION



The blended glazes are quickly and efficiently applied with a syringe, to a number of assessment tiles, to be fired under different conditions. Hereafter you handle 35 glazes as easily as one for kiln packing, unpacking, mounting labelling etc.



STACKED FOR FIRING



A stack of tiles (from different sets) propped apart by kiln wadding is ready to be placed into the kiln. Taking up less volume than a household brick, it's easy to obtain virtually identical firing conditions for hundreds of glazes at once.
Assessment tiles can be used anywhere you wish to subject a large number of glazes to the same firing conditions including special cases such as draw trials.

cones are placed next to the stack.

Once you get some fired results with the assessment tiles, you will start to get ideas on glazes you wish to explore more closely. This is done with the 'Individual Tiles'.

Individual Tiles

I recommend you do a complete set of 35 tiles for at least one of the 8 sets covered here -- perhaps the 0.8 Limestone Set would be best since it is a kind of central point for the whole series. You can either fire all 35 glazes to the same temperature, or fire different areas of the grid to appropriate temperatures as suggested by your assessment tile results.

Glazing and Firing the Individual Tiles

1. Using iron oxide, write numbers 1 to 35 on the *backs* of the tiles and dip the bottom 1 cm in wax (see Diagram 6.3).

2. Dip each tile full face in its glaze. The glaze should be stirred (preferably with a finger) just before dipping. This first layer of glaze should be fairly thin, say half a millimetre or so. Carefully dip the top half of the tile a second time. The second dipping should give a total thickness of glaze about 1½ mm thick.

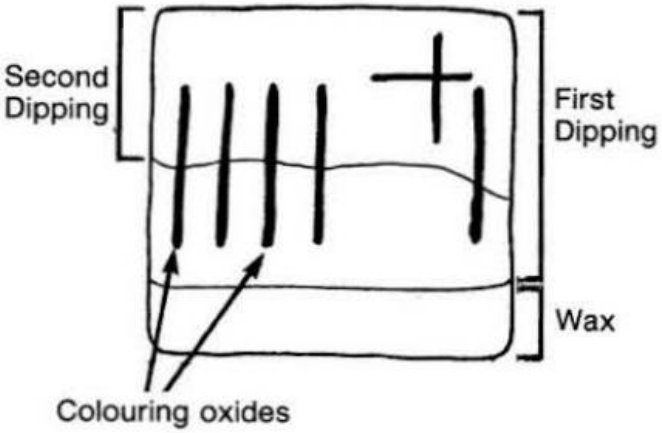
3. Apply thin brushstrokes of the colouring oxides as shown in Diagram 6.3. There is no point in trying to get all the colouring oxides on; the tiles are not big enough. If working in a group, I would recommend that everyone use cobalt, copper and iron oxides, you can decide which of you will apply which optional colouring oxide and opacifier. Everyone should have five oxides, as per the diagram, *with a space left for unadulterated glaze.* The optional colouring oxides are any others that you want to try. Of the opacifiers, titanium oxide (and rutile) are quite rewarding. Tin oxide sometimes causes chrome/tin pinks if you have chrome oxide in the kiln. Bone ash and zircon seem to be less interesting in this application. I suspect they really need to be more thoroughly mixed with the glaze.

Set the glazed 'individual tiles' vertically in a large slab or slabs of kiln wadding clay and fire with the appropriate cone(s) alongside.

PUTTING THE RESULTS IN ORDER

Results should preferably be mounted especially the individual test tiles that are part of a larger set. Remember that a great advantage of doing a systematic course such as this is that one can get to understand glaze principles by seeing the relationships between different related glazes. To see these connections, the material and the data *must be presented in order.* The attention you give to this matter will pay dividends in your quest for understanding of causes and effects. So I would suggest individual tiles be mounted on stiff card or board in the order as seen in the alumina/silica diagram, and that as much data as possible be presented right with the tiles. Because of the large volume of tiles produced in this course, it is vital that this seemingly minor aspect be attended to promptly after each firing, *otherwise chaos will reign,* and vital information will be lost. See more suggestions in Chapter 4 under 'Labelling Test Tiles and Recording Data'.

DIAGRAM 6.3 — Individual Tile

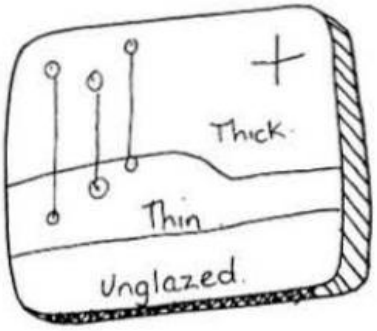


Notes:

1. Use very little cobalt oxide thinned out with plenty of water until it leaves a pale grey mark when brushed onto the glaze.
2. Manganese dioxide needs to be fairly thick, and iron oxide too.
3. Add about 5%-10% ball clay to your water/oxide suspensions if they tend to peel off the glaze.

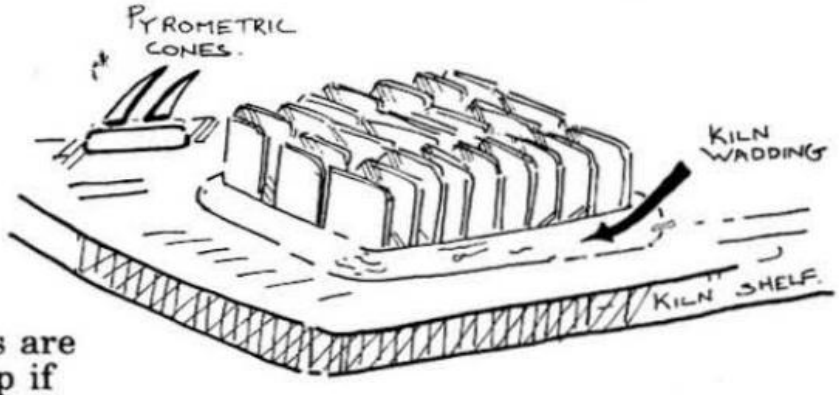
Individual Tiles

After seeing the results of a stack of assessment tiles fired, you can decide what glazes are worth further investigation in a similar firing.

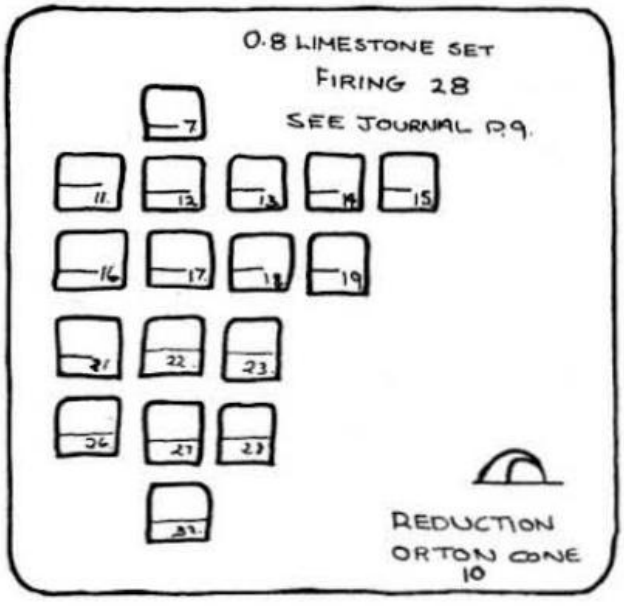


Apply the glazes to individual tiles, numbers on the back, apply colouring oxides, and fire vertically, in serried ranks.

FULL SIZE INDIVIDUAL TILE.



After firing, the tiles are separated, cleaned up if necessary, and mounted in order on board, along with necessary information.



ASSESSMENT OF RESULTS

Beautiful and striking glazes will often be evident as soon as the tests are taken from the kiln, but once you have all the results and data *in order,* you are ready to start really learning about glazes. A hand lens is really necessary to see finer detail. Some of the features to be observed are as follows:

1. The glazes have a wide range of melting points. In any one set, the glazes that melt first include the 'eutectic' or part of an eutectic trough. (See Chapter 13 on eutectics.)

2. Some glazes are shiny, some matt, and these properties do not necessarily have anything to do with glaze maturity. Many mature and even runny glazes are matt because of crystals forming in the cooling cycle. Some glazes become 'shiny' before reaching full maturity, e.g. some high silica glazes, referred to in the Results Charts as 'sugary'. Types of mattness vary enormously, both in appearance and in usefulness, e.g. some are excellent for domestic pottery. Some are easily marked by cutlery, or hard to clean, or make a sound with cutlery that some people dislike. Some are quite useless for domestic pottery, but because of their exceptional beauty, are widely used in non-functional work.

3. Some glazes are transparent and some opaque. Although it is often stated that matt glazes are necessarily opaque, you will find many are semi-opaque at most. Types of opacity in these base glazes varies greatly, some being very white, some off-white, or even coloured. Opacity is sometimes even, sometimes textured — semi-opacity might take the form of light frosted glass, or sometimes a mottling of opaque crystals is suspended in a clear glass matrix.

4. Sometimes quite dramatic crystals will form in a glaze.

5. Some glazes are crazed, some not. The crazing varies from set to set and varies greatly depending on what body is used. In general, for any one set on any one body, crazing may be decreased by increasing alumina *and/or* silica, but the relative importance of alumina versus silica depends on the set under consideration, and also the temperature the set is fired to. To detect crazing that is hard to see the tile can be stained with ink, or alternatively examined with a hand lens with a bright light source, the tile being held so it is almost parallel to the direction of the light.

6. Most glazes give a different effect depending on thickness, unless they are very stable and opaque. Sometimes the difference is simply a matter of the optics of thick versus thin glass, but often there is a difference brought about by interaction between clay and glaze, the 'clay-glaze interface' (see Chapter 17), so that the thin glaze is actually higher in some body component than the glaze applied thickly. The ingredient supplied by the body may be alumina or silica, or something like iron or titanium oxides.

7. Bubble content varies enormously depending on glaze composition and degree of maturity. The size and number of tiny bubbles is vital to the appearance of certain glazes, e.g. celadons.

8. The colours obtained from a colouring oxide will vary greatly depending on the base glaze used, the clay body and the firing schedule.

9. Some base glazes develop significant colour without adding colourants to either glaze or body, for example, Chun-blue and a matt pink that occurs along the kaolin baseline in most of the sets studied here.

10. Application of spots or stripes of colourants over and/or under the glazes will obviously give an indication of how the colourant will act as a pigment when applied with a brush etc.; however, if the application is reasonably heavy, careful study of the borders of the spot or stripe with a hand lens will often reveal a microscopic 'line blend' of what to expect with increasing addition of the colourant to the glaze batch.

11. To resolve a theoretical point, you may sometimes wish to see detail beneath the surface of a glaze. If it is opaque, you can cut the surface back with emery stone or a grinder. Wet the surface before examining it with a hand lens.

12. Occasionally there is a big jump in properties from one glaze to another; you may wish to study these areas in more detail with samples closer together.

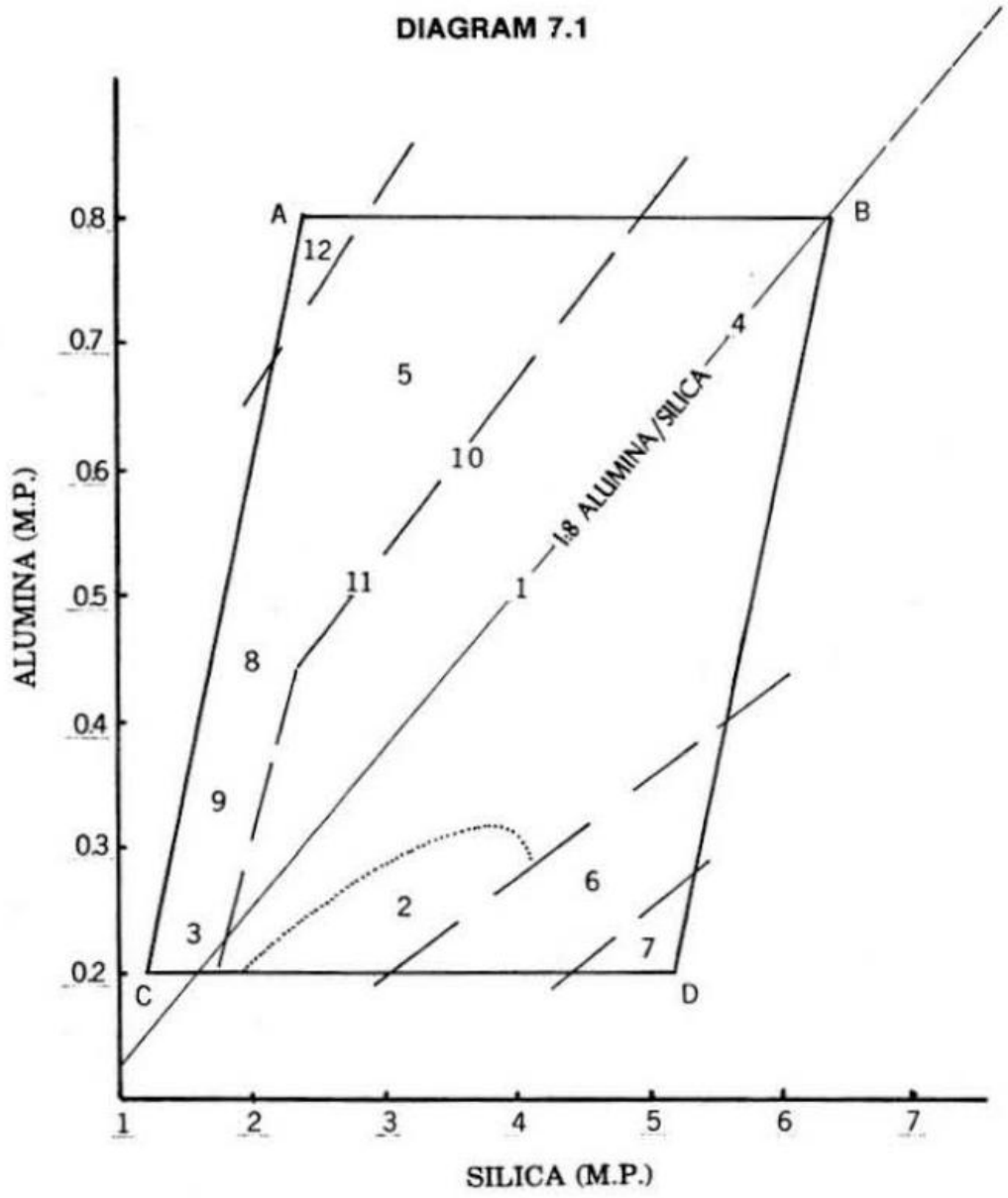
7 ALUMINA and SILICA in STONEWARE GLAZES

Before considering the differences between the different sets of glazes, it is useful to consider the similarities; this naturally leads us to look at the roles of alumina and silica in stoneware glazes. We need consider the fluxes here in general terms only; the roles of each particular flux will be considered when discussing the individual sets.

EFFECTS OF VARYING ALUMINA AND SILICA

A number of features seem to occur regularly on all or most of the sets, and these are discussed below with reference to the different zones drawn on the diagram. See Diag. 7.1.

DIAGRAM 7.1



1. SHINY GLAZES

When the sets are adequately matured, clear shiny glazes occur in a wide band (Zone 1) on either side of the 1:8 alumina/silica ratio line. However, around corner C, the glazes tend to be runny and crazed, while around corner B, the high alumina high silica content causes them to be very stable and uncrazed, with a degree of opacity creeping in. Furthermore in Zone 2 within the shiny zone, there is a tendency towards opalescence at higher temperatures.This is a type of 'Chun' glaze that often occurs in this region if the temperature is just right. If the temperature is too high, it goes clear, if too low, it remains opaque and sometimes matt. These glazes usually have an alumina/silica ratio of about 1:12.

In Zone 3 around corner C, you often get development of large crystals. In this case, low alumina is important.

Zone 4, the stable uncrazed glazes mentioned before, is a good source of glazes for 'whiteware', or anywhere where a clear, uncrazed and mechanically strong glaze is required. By 'whiteware' I am particularly referring to pottery that uses brushwork of cobalt, iron etc. over a white clay or white slip. Because of the stability of these glazes, the oxide patterns come out of the firing exactly as they went in.

2. MATT GLAZES

In corner A, with high alumina and low silica, there are the alumina matt glazes, a commonly used and stable form of matt glaze. (See Zone 5.) The matting is caused by microscopic crystals forming in the glaze mostly during the cooling cycle, so the rate of cooling will often affect considerably the mattness of these glazes. With even more alumina, a dry alumina matt is achieved as a result of incomplete fusion; this effect will often occur on or near Glaze No. 1 (Zone 12) in many of the sets. To the extent that the mattness is caused by incomplete fusion (as opposed to crystallisation), it will not be affected by rate of cooling. The clay content of such glazes is usually high, and they therefore lend themselves to raw glazing; used on bisque ware, the high clay content may cause crawling unless some of the clay is calcined. The calculation enabling you to replace raw clay with calcined without altering the glaze composition is given in Chapter 14.

A stippled 'orange-peel' surface is not uncommon on a wide variety of glazes, but is often fugitive. There are reliable orange-peel glazes, however, that occur in Zone 10 along the boundary between the shiny and matt glazes, in most of the sets studied here. The effect varies from a few pinpricks in a shiny glaze through (as you increase alumina and decrease silica) to a rich textured matt, then to where the texture is no longer visible giving a normal alumina matt. As the shiny/matt boundary moves with increasing temperature, so the effect moves from glaze to glaze. The effect seems to be caused by tiny bubbles coming to the surface and bursting but not smoothing over completely. In the more fluid 'shiny' glazes the bubbles heal over completely after bursting to give a high shine; while presumably in the very viscous high alumina glazes, the bubbles tend to remain trapped in the glass. Remember that alumina is a glass 'stiffener', so it follows that the glazes that are higher in alumina will show evidence of increased viscosity.

On several of the sets of glazes, there occurs adjacent to this 'orange-peel' effect, an area where surface crystallisation is just large enough to be seen, and this effect seems to combine with the bubble effect to give a beautifully rich semi-matt surface (Zone 11). Both zones have the same ratio of alumina to silica, but the 'crystalline' orange-peel is higher in fluxes.

Flux-alumina Matts — In Zone 8 in the Barium Set and the high Limestone Sets, flux-alumina matts occur. Under the right conditions, these glazes can produce interesting stable colour matt glazes, sometimes exhibiting 'colour break'. A widely used glaze of this type contains equal parts of whiting, kaolin and feldspar.

Flux Matts — These glazes, indicated by Zone 9, are less stable, often very runny, often developing 'stringing', i.e. rivulets of glaze flowing down the pot, the glaze often being shiny or matt depending on thickness, often with lots of small crystals. Natural ash glazes are often of this type, typically high in calcium, low in alumina and silica.

Matt Pink Glazes along the Kaolin Baseline — When fired in strong reduction, most of the sets under study developed matt pink glazes along the kaolin baseline (i.e. between A and C) or near it. As the glazes are fired higher, the effect disappears as the glazes become shiny; the pink does not occur if glaze application is too thin. It often occurs in association with

grey staining, which might be carbon inclusion as a result of a strong reduction firing.

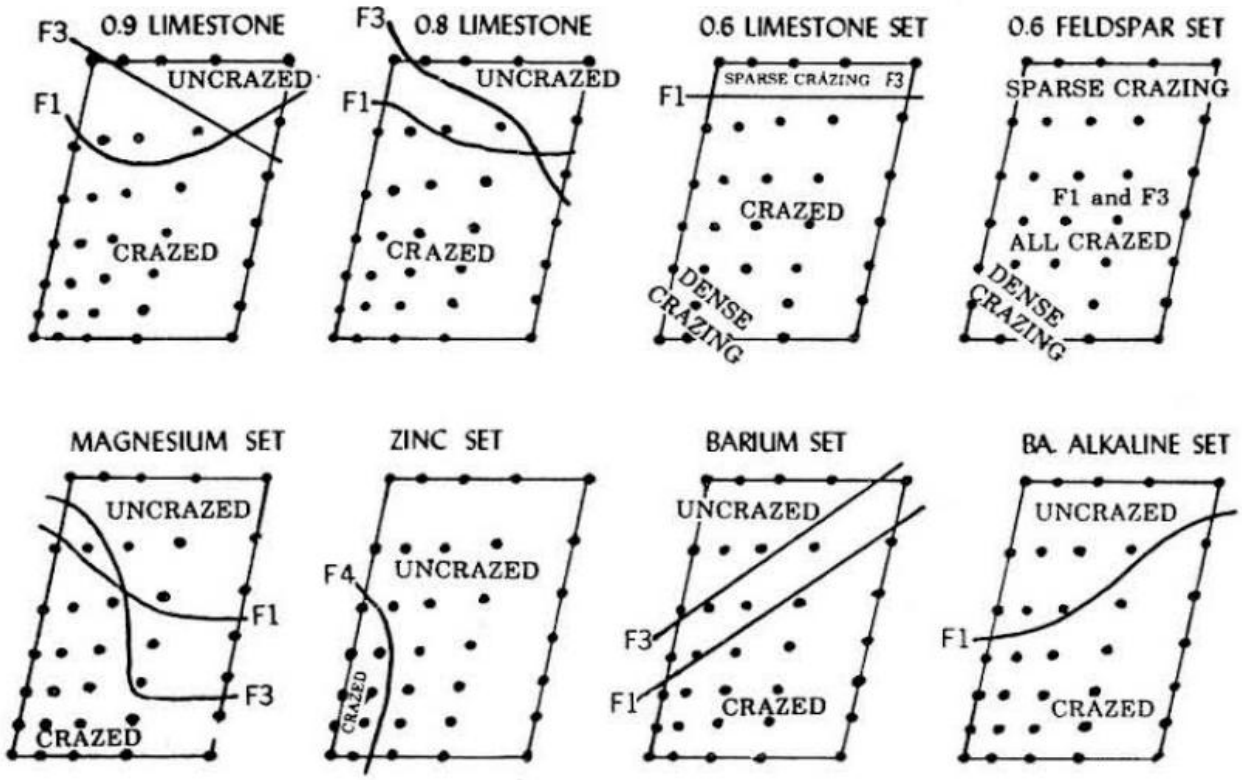
3. HIGH SILICA GLAZES

Most of the sets have a fairly sharp transition from shiny glazes (Zone 1) to underfired high silica glazes (Zone 7). There is usually a narrow band of 'sugary' semi-matured glazes (Zone 6) just before the really underfired ones. Sometimes at lower temperatures the transition is not so sharp, e.g. the Magnesia Set and the 0.8 Limestone Set can produce a useful range of opaque matt glazes (including Zone 2 and Zone 6) in this area — see individual sets to follow.

4. CRAZING

The relative roles of alumina and silica on crazing depends a lot on the fluxes. For example, the Barium Set shows that crazing increases as silica increases, whereas the reverse is the case in the Zinc Set and other sets at high temperature. In all the sets studied here, decreasing both alumina and silica (i.e. increasing the fluxes — moving towards corner C) causes increased crazing. The effect of temperature is interesting. In the Magnesium Set and the high Limestone Sets, higher temperature causes increased crazing in high alumina glazes and decreased crazing in high silica glazes. See Diagram 7.2.

DIAGRAM 7.2 - Crazing



Notes:

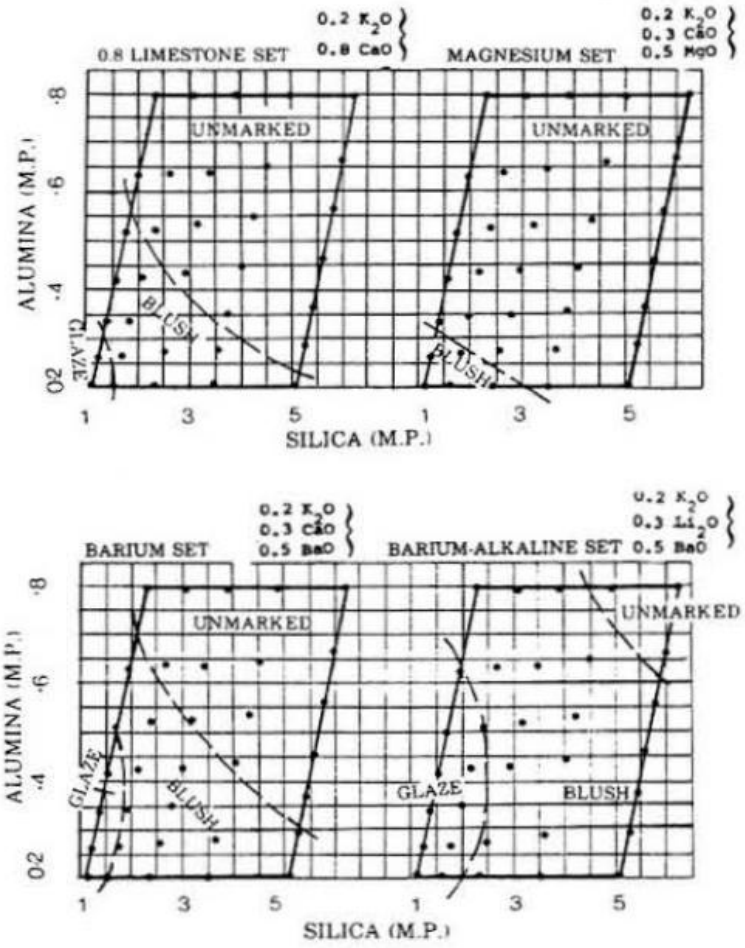
1. Clay body used is Podmore's Porcelain. Many normal stoneware bodies will craze less than shown here.
2. Marginally uncrazed glazes may craze with time e.g. months or years. They may also craze if applied more thickly, or over a larger area. The results given here were taken from normal assessment tiles about one month after firing.
3. F1 = Firing No. 1 etc.

A more complete discussion of glaze fit is given in Chapter 19.

5. VAPORISATION OF FLUXES

If the assessment tiles are fired in stacks, each set of glazes leaves a vapour 'imprint' on the back of the tile above. Alternatively, close examination of the unglazed body adjacent to the glaze will give the same information. The imprint is usually evident as an apricot-coloured blush on the clay, or when exceptionally heavy, as a clear glaze on the porcelain. Some of the results are predictable, some not so — see Diagram 7.3:

DIAGRAM 7.3 - Vapour Imprint Diagrams



Notes:

1. These diagrams are compiled by observing the reverse sides of porcelain assessment tiles fired in stacks, the vaporising fluxes from the glazes of one tile leaving an 'imprint' on the back of the tile above. This is a crude but simple technique for comparing in different glazes the vaporisation caused by an overload of fluxes.
2. Areas marked 'glaze' on the diagrams are where the fluxes are so volatile as to produce a clear vapour glaze on nearby unglazed porcelain.

Some of the observations made from the tiles are as follows. (See Diagram 7.3).

(a) In all sets vaporisation is heaviest in corner C (high fluxes) and tapers off as does the flux content. Compare the Vapour Imprint Diagrams with the corresponding Recipe Charts or the Oxide % Charts.

(b) Vaporisation seemed almost as heavy in oxidation as reduction, but much less obvious, because of the much richer apricot colour produced in reduction.

(c) Lithium and barium vaporise very readily, calcium less so, and magnesium least of all. Zinc is a special case.

(d) When the Zinc Set is fired in strong reduction, zinc oxide seems to disappear without trace (see 'Zinc Set' later) but in oxidation, there seems to be vaporisation from virtually all of the glazes, evident as a colourless sheen on the porcelain around virtually all of the glazes, visible only if a bright light is reflected off the surface.

SOURCES OF ALUMINA IN GLAZES

Most of the alumina for our glazes comes from feldspar and various clays. Several of the other sources of alkali that we sometimes use instead of feldspar also introduce alumina, e.g. nepheline syenite, Cornish stone, frits etc. When we use these materials, we are probably more concerned with the alkalis than with alumina; when we specifically want alumina alone, we must use alumina hydrate or its calcined equivalent, pure alumina. If we do not mind a little silica being introduced as well, we will probably use a clay, such as kaolin. So putting this into some sort of order, our main sources of alumina are as follows: (Table 1)

SOURCES OF SILICA IN GLAZES

As well as the relatively pure forms of silica (to follow), silica is introduced into glazes in feldspars, nepheline syenite, frits, Cornish stone, all clays, and from many other sources.

Relatively pure silica occurs in a number of different forms:

a. *Crystalline Silica*
The most common form is quartz, which may occur as reef quartz or as quartz sand, and also as quartz sandstone. Silica from reef quartz and quartz sands are freely available in Australia and are usually of high purity. You need silica of 200 mesh or finer for your glazes.

b. *Microcrystalline Silica*
Especially flint, also chert, chalcedony, agate, onyx, jasper and others. Flints are fairly widely distributed in Australia but not readily available commercially. One can usually substitute 'silica' for 'flint' in a glaze recipe without affecting the results noticeably. The main differences noted in the literature are:
(i) silica in a glaze has a slightly greater tendency to cause crazing than flint and
(ii) flint has a significantly lower specific gravity and is, therefore, more easily suspended in a slip.

c. *Amorphous or Non-Crystalline (Colloidal) Silica*
(i) Opal ($SiO_2.nH_2O$)
This includes precious opal, common opal, diatomaceous earth and others. The water content varies, hence the 'n' H_2O. I guess we will leave out precious opal as a glaze ingredient, but common opal and diatomaceous earth are both potential sources of colloidal silica, the latter being readily available from rock millers and pottery suppliers. These forms of silica are not used very much in glazes, though I know of both of them being used in the production of Chun glazes. If you read what Bernard Leach has to say on Chun glazes, you will find that he considered colloidal silica

Table 1. Common Sources of Alumina

Feldspars	e.g. $K_2O.Al_2O_3.6SiO_2$	
Nepheline syenite	e.g. 0.25 K_2O 1.1 Al_2O_3 4.65 SiO_2 0.75 Na_2O	(fairly variable)
Cornish stone	e.g. 0.5 K_2O 0.25 Na_2O 1.2 Al_2O_3 8.4 SiO_2 0.25 CaO	(fairly variable)
Kaolin	e.g. $Al_2O_3.2SiO_2.2H_2O$	
Ball Clays	e.g. 0.3 $RO.Al_2O_3.5.0SiO_2$	(*very* variable)
Other Clays		
Alumina Hydrate	$Al_2O_3.3H_2O$	
Alumina	Al_2O_3	

Note: If possible, we usually try to avoid putting the alumina into the glaze as 'Alumina' or 'Alumina Hydrate' mainly because of the difficulty of incorporating these materials into the glaze, especially in a quick firing.

important in the production of Chuns. However, he was referring to colloidal silica from plant ashes.

(ii) *Vegetable Ash*
The silica that is present in wood ash, grass ash etc. is colloidal silica. Grass ashes are especially high in silica, e.g. rice straw ash, which is widely used in the orient as a glaze ingredient, commonly contains 80% SiO_2. As mentioned, grass ash or wood ash is often used as the source of silica in Chun glazes. Syncarpia (turpentine) species have a high silica content in their wood ash, e.g. 80%. They are a fairly common tree in Australian wet sclerophyll forests.

Table 2. Common Sources of Silica

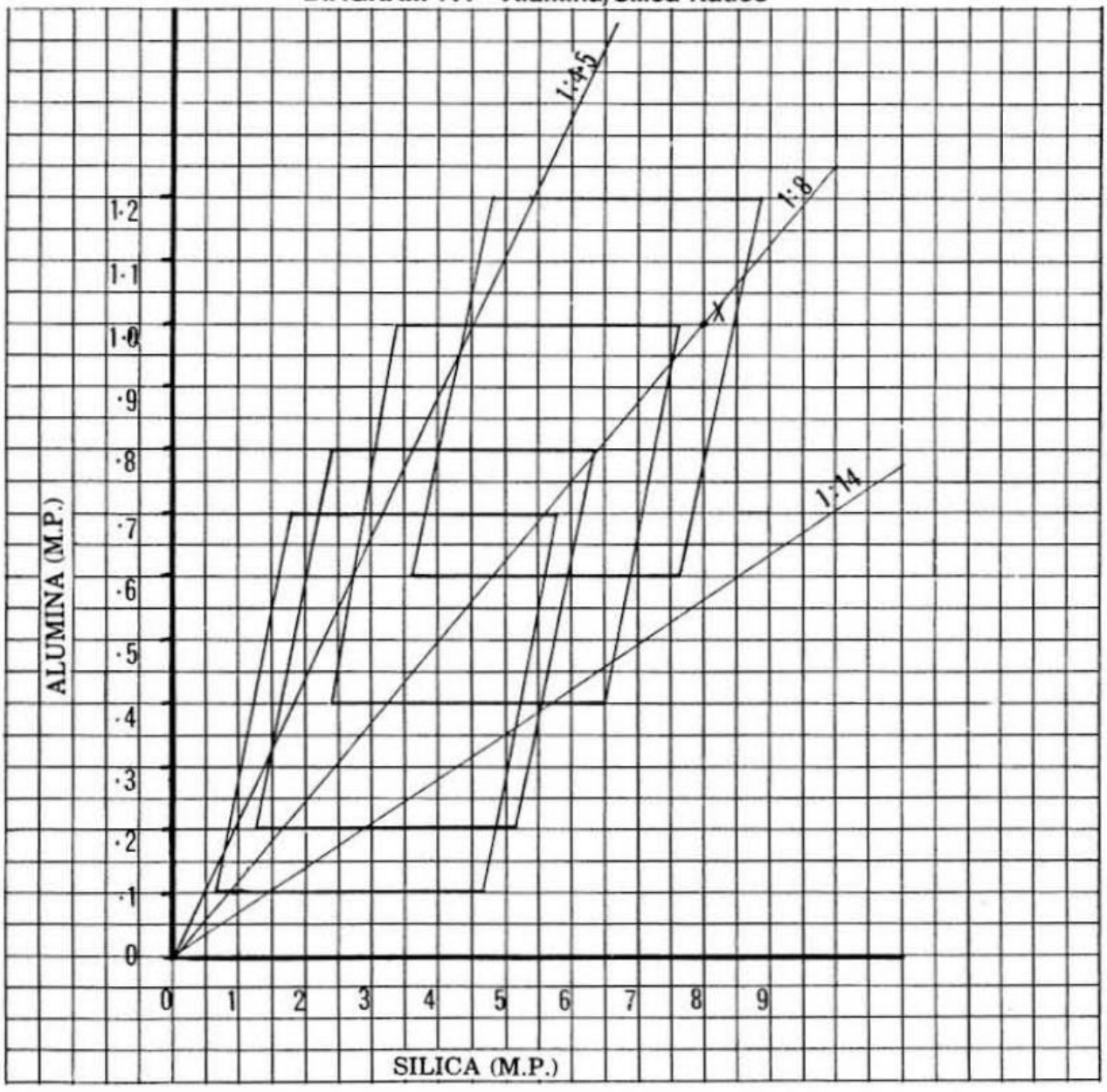
Silica
Flint
Diatomaceous earth and common opal
Grass ash, wood ash etc.
Cornish stone
Feldspars
Nepheline syenite
Frits etc.

THE ALUMINA/SILICA RATIO

If you look at Diagram 7.4 you will see how the sets of test glazes fit onto the larger alumina/silica graph. See Diagram 7.4.

When you get the hang of using molecular formulae to express glazes, you will often find it useful to roughly calculate in your head the alumina/silica ratio. A starting

DIAGRAM 7.4 - Alumina/Silica Ratios



point sometimes used when teaching stoneware glazes is a 'Standard Cone 9 Limestone Glaze'. In this glaze with 0.5 M.P. Al_2O_3 and 4.0 M.P. SiO_2, the alumina/ silica ratio is obviously 0.5:4.0. So that we can compare one ratio easily with another, we usually bring the alumina to unity. This is done simply by dividing both numbers in the ratio by the alumina number (M.P.). Thus if we take the original ratio: 0.5:4, and divide both numbers by 0.5, the ratio now reads 1:8, which is just using more convenient numbers to express exactly the same ratio:

Original figures	-- 0.5	:	4
Divide both by 0.5	-- $\frac{0.5}{0.5}$	:	$\frac{4}{0.5}$
Equals	-- 1	:	8

If you plotted all the glazes with alumina silica ratios of 1:8 on the graph, you would get the line I have drawn in Diagram 7.4 extending out from the zero point, and passing through Point X at 1.0 Al_2O_3, 8.0 SiO_2. (Note that the 0.5:4 point falls on this line.) If you look at the 'Results Charts' given for the individual sets of glazes later, you will see that the 1:8 line runs straight up through the middle of the zone of clear shiny glazes once the set is adequately mature. Glazes with alumina/ silica ratios around 1:4 or 1:5 can be regarded as 'high alumina' glazes (by comparison with the 1:8 line) and will often be matt or semi-matt. On the other hand, glazes with alumina/silica ratios of 1:14 or more can be regarded as 'high silica' glazes. Sometimes this will give you an opaque glaze, the excess (unfused) silica being the opacifier. Often, however, the result is simply an underfired glaze. But the point to note is that the *ratio* gives you a better guide to the nature of the glaze than does the molecular parts figure for either alumina or silica. For example, if you look at most of the well matured sets you will see that 0.7 M.P. alumina can give a matt glaze, a shiny glaze, or an underfired glaze, depending on the amount of silica present. However in the same set, virtually all the glazes with 1:8 alumina/silica ratio are shiny, transparent glazes, all with 1:4.5 ratio are matt, and many with 1:15 ratio are sugary or underfired. This sort of pattern you will find repeated again and again.

8 LIME ALKALI GLAZES

The four sets of glazes investigated in this chapter have varying amounts of lime (from calcite) and alkali (from K-feldspar). An intermediate set is presented as data only. The fluxes of these five sets, expressed here as molecular parts, are as follows:

0.9 Limestone Set

0.1 K_2O
0.9 CaO

0.8 Limestone Set

0.2 K_2O
0.8 CaO

0.7 Limestone Set (data only)

0.3 K_2O
0.7 CaO

0.6 Limestone Set

0.4 K_2O
0.6 CaO

0.6 Feldspar Set

0.6 K_2O
0.4 CaO

THE USE OF CALCIUM IN STONEWARE GLAZES

Calcium oxide (calcia or lime) is a strong flux in stoneware glazes and is one of the most commonly used stoneware fluxes (usually with a little K_2O) because of the benefits it imparts, including making the glazes more stable, reliable, less sensitive to odd variables in the kiln. This reliability over a wide range of compositions and firing conditions is responsible for its being perhaps the main flux in a large range of 'middle-of-the-road' stoneware glazes. It may cause more responsive behaviour, however, if used in excess. Although it normally acts as a flux, increased addition of calcium oxide will (as with any ceramic materials) eventually have the opposite effect, so that the melting point of the glaze is rising as you add more. This process of overloading the glaze is accompanied by the formation of very small crystals of anorthite ($CaO.Al_2O_3.2SiO_2$) and also wollastonite ($CaO.SiO_2$). This is a very common way of obtaining matt glazes and includes calcium matts and calcium-alumina matts.

Calcium oxide has an important role in glazes containing iron oxide. The effect of iron as a colourant is largely determined by whether the iron is dissolved in the glaze or crystallises out. Calcium oxide is very effective in dissolving the iron. This is discussed in more detail in Chapter 20.

SOURCES OF CALCIUM

1. Calcium carbonate ($CaCO_3$) occurs in nature in several forms important to the potter:
a. limestone (or calcite)
b. marble
c. chalk and others.
The whiting that we use in our glazes is usually ground calcite and is typically fairly pure (around 99%). Calcium carbonate, having a relatively low specific gravity, readily remains in suspension in the glaze slip and assists in keeping heavier materials suspended.
2. Dolomite ($CaCO_3.MgCO_3$) will be covered in magnesia glazes.
3. Wollastonite ($CaO.SiO_2$) is a commonly occurring mineral which is available from pottery suppliers fairly cheaply. In his book *Oriental Glazes*, Nigel Wood recommends it over whiting for the production of more authentic Chinese glazes.
4. Wood ash is often high in CaO. According to Cardew *Pioneer Pottery*, page 54, Applewood ash contains 70.9% CaO, and tallowwood (eucalyptus microcorys) contains 52% CaO. Herbert Sanders in his book, *The World of Japanese Ceramics*, gives on page 239 a recipe for 'synthetic common ash', which when used by itself, gives a very 'ash-like' glaze. It contains 62% limestone. Its molecular formula is:

.031 K_2O
.88 CaO 0.087 Al_2O_3 0.37 SiO_2
.084 MgO

which as you can see is mostly CaO and little of anything else.

THE USE OF ALKALI FLUXES IN STONEWARE GLAZES

The alkali fluxes are those of the R_2O type, i.e. K_2O, Na_2O and Li_2O. For very practical reasons, it is unusual to find stoneware glazes with no alkali content. All the glaze sets studied in this course on base glazes have some alkali fluxes. Although compounds of potassium, sodium and to a lesser extent lithium abound in nature, many of these compounds are water soluble and, therefore, not very useful to us unless we want to get into making our own frits. Lithium carbonate is relatively insoluble and is often used as a glaze ingredient. The main sources of insoluble K and Na are various feldspars, nepheline syenite, Cornish stone etc., all of which introduce lots of alumina and silica along with the alkali. Commercial alkaline frits are available. Occasionally small amounts of soluble alkali compounds (such as salt, NaCl) are introduced for some specific effect.

The alkalis are strong fluxes and will increase the fluidity of the molten glaze. Certain unique colours are developed well in alkaline glazes. They tend to increase the brilliancy of a glaze. Highly alkaline glazes tend to be more easily scratched, and prone to weathering, in extreme cases (e.g. with very low alumina and silica) to the point where the fired glaze is actually soluble in water. Na_2O and K_2O have high coefficients of thermal expansion and, therefore, tend to cause crazing, while Li_2O is just the opposite. The amount and type of alkali are going to strongly affect glaze fit characteristics.

With regard to physical and chemical properties, it is usually found that a *mixture* of alkalis will give more optimum results than the use of any one alkali alone. As most of our feldspars, nepheline syenites etc. already contain a mixture of K_2O and Na_2O, this is no problem unless you are after some specific combination.

Comparison of Na and K:

According to Parmelee, the substitution of potassium for sodium in sufficient quantity in glazes has the following effect:

1. increases the brilliance
2. decreases the fluidity
3. increases scratch hardness
4. increases resistance to solution by water
5. decreases the coefficient of expansion
6. causes some changes to colour response from colouring oxides.

In the eight sets of glazes studied here, the role of alkalis can be assessed in two ways: firstly from the four sets that have varying amounts of K_2O and CaO as fluxes, and secondly from the Barium-alkaline set, and to a lesser extent, the Barium Set (BaO acts in some ways like an alkaline flux). Although we often lump the alkali fluxes together (disregarding lithium, we refer to them as KNaO) for the purpose of comparing them with and separating them from the non-alkali fluxes (RO type), Parmelee warns that wholesale substitution of one alkali for another can have a strong effect in a highly alkaline glaze, especially when using colourants.

SOURCES OF ALKALIS

With the exception of salt and borax, I will deal only with the insoluble ones.

Sodium

1. Soda feldspar
See under 'Raw Materials' in Chapter 1.
2. Nepheline syenite
3. Cullet. This is crushed bottle glass or window glass, and is of variable composition. Parmelee gives the following approximate composition for cullet:

$$\begin{matrix}0.5\ Na_2O \\ 0.5\ CaO\end{matrix}\ 1.0\ SiO_2$$

You would probably be stabbing in the dark, however, unless you got your cullet and analysis direct from the manufacturer. Crushed glass could be ground to a suitable fineness in a ball mill.
4. Alkaline Frits e.g. Podmore's P.2250, and Ferro Frit 3110. See under 'Raw Materials' in Chapter 1.
5. Salt (NaCl). This is widely used in the salt-glazing process, which is not covered in this course. Although it is highly water soluble, salt is also used in small quantities in some special glazes for special effect, e.g. in Shino type glaze, to help bring out the orange-brown colour. Salt has the ability to volatilise iron from clays and glazes. It combines with the iron to form the very volatile compound, ferric chloride.
6. Borax ($Na_2O.2B_2O_3.10H_2O$) is water soluble and only rarely used as such in stoneware glazes.

Potassium

1. Potash feldspar — see under 'Raw Materials' in Chapter 1.
2. Cornish stone (Cornwall stone) is of more importance to British potters, who

use it as their prime source of alkali. It is an altered pegmatite or granite rock and is fairly variable in composition. If you want to use it accurately in a glaze formula, you would need to have an analysis for the 'Cornish stone' you are using. However, the following might be considered typical (See Parmelee for original figures):

0.5 K_2O
0.25 Na_2O 1.15 Al_2O_3 8.5 SiO_2
0.25 CaO 0.04 F_2
with traces of Fe_2O_3 and MgO

See also the recommended texts by Fraser or Hamer for more on Cornish stone.

Lithium

1. Lithium carbonate (Li_2CO_3) is the main source of lithium for the studio potter, however, it is very slightly water soluble and relatively expensive.

All the following tend to vary significantly from the theoretical formula and are not always easily available.

2. Petalite (theoretically $Li_2O.Al_2O_3.8SiO_2$) is lithium feldspar. It is either difficult to obtain or expensive in Australia.

3. Lepidolite (theoretically $LiF.KF.Al_2O_3.SiO_2$) is lithium mica.

4. Amblygonite (theoretically $LiAlFPO_4$) occurs near Darwin (NT). It promotes rapid fluxing and high gloss. The large content of fluoride and phosphoric oxide makes it particularly useful in opaque glazes.

5. Spodumene (theoretically $Li_2O.Al_2O_3.4SiO_2$).

PRELIMINARY COMMENTS ON EXPERIMENTS

Data, Firings, Materials and Results

(*Note:* These comments apply to the eight experiments detailed in Chapters 8, 9, 10, and 11.)

1. Data

The recipe and oxide weight % data is given to 2 decimal places, but for most practical purposes, the decimals can be ignored, and there will be no detectable difference. The decimals are given for mathematical reasons only; if doing a sequence of calculations, rounding off each time to the nearest unit, it is possible for the discrepancy to be compounded rather than to cancel out. A significant error will then appear which, if nothing else, may cause concern when crosschecking results. One of the advantages of this course is that multiple crosschecking is possible because of the systematic relationships between glazes.

2. Recipe Charts and Oxide Weight Charts

These charts are just another way of presenting the information listed in the Data Sheets but showing more clearly the relationships that exist. The Recipe Chart consists of a normal baseline grid (based on molecular parts) with part of the corresponding recipe triaxial (based on weight parts) superimposed. Similarly the Oxide Weight Chart has part of the corresponding oxide weight triaxial superimposed. For the benefit of potters more familiar with the triaxial format the 2 triaxial diagrams (P. 46) show how the recipe chart and the oxide weight chart for the 0.8 Limestone Set would be plotted on triaxial paper – exactly the same information presented on a different framework.

3. Results Charts

Where the zone boundaries (between 'shiny' and 'matt', for instance) are indicated by a broken line, this indicates very little change from one glaze to the next across the boundary. A boundary line passing through a dot (a glaze) indicates that glaze is intermediate in properties between the two zones. A circle around a dot indicates that glaze exhibits an 'orange-peel' surface. Where the effect is only slight, this is represented by a broken circle. To get a full appreciation of the results, it is necessary to read the comments on the page facing the results charts.

DIAGRAM 8.1

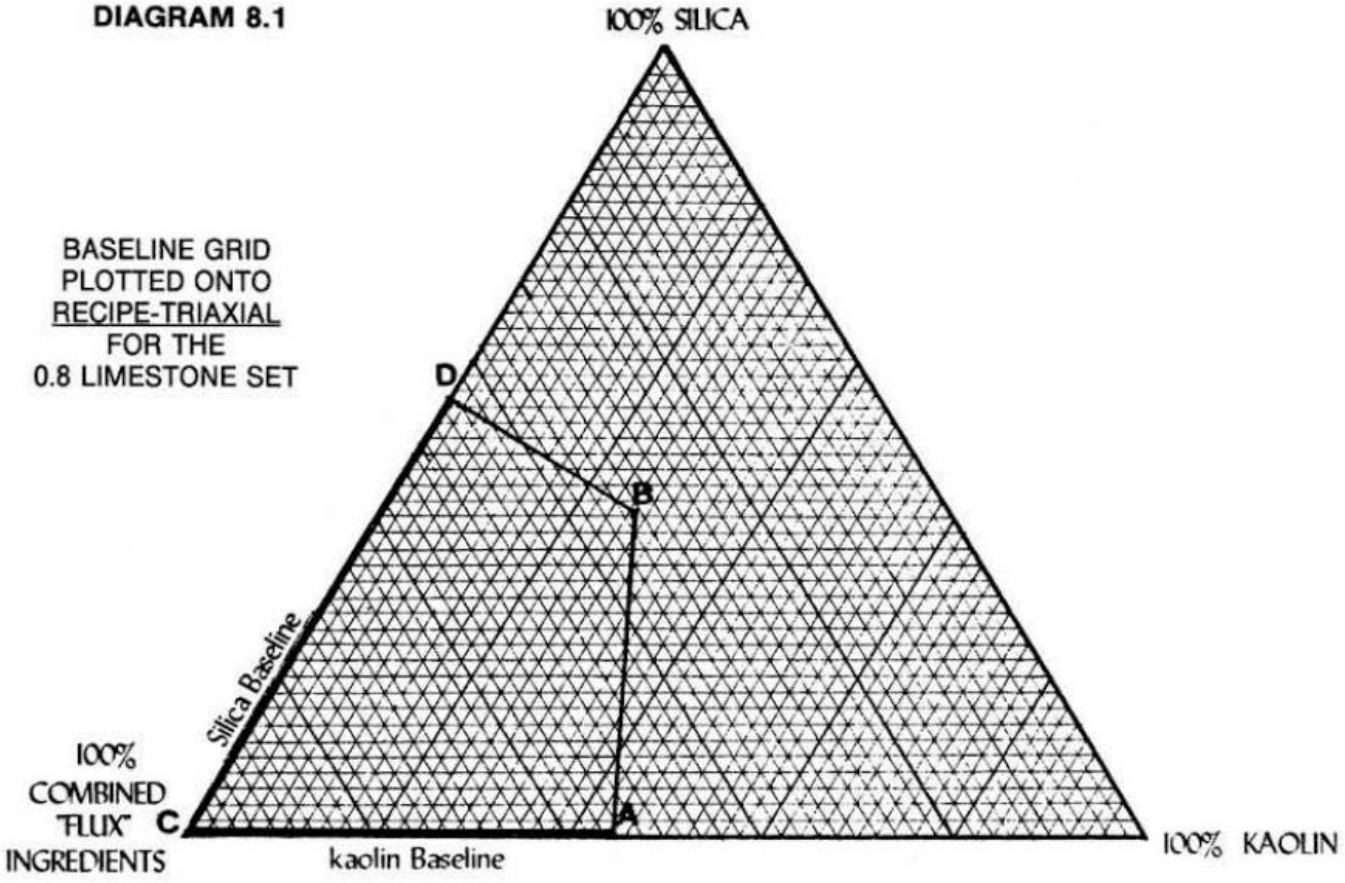


DIAGRAM 8.2

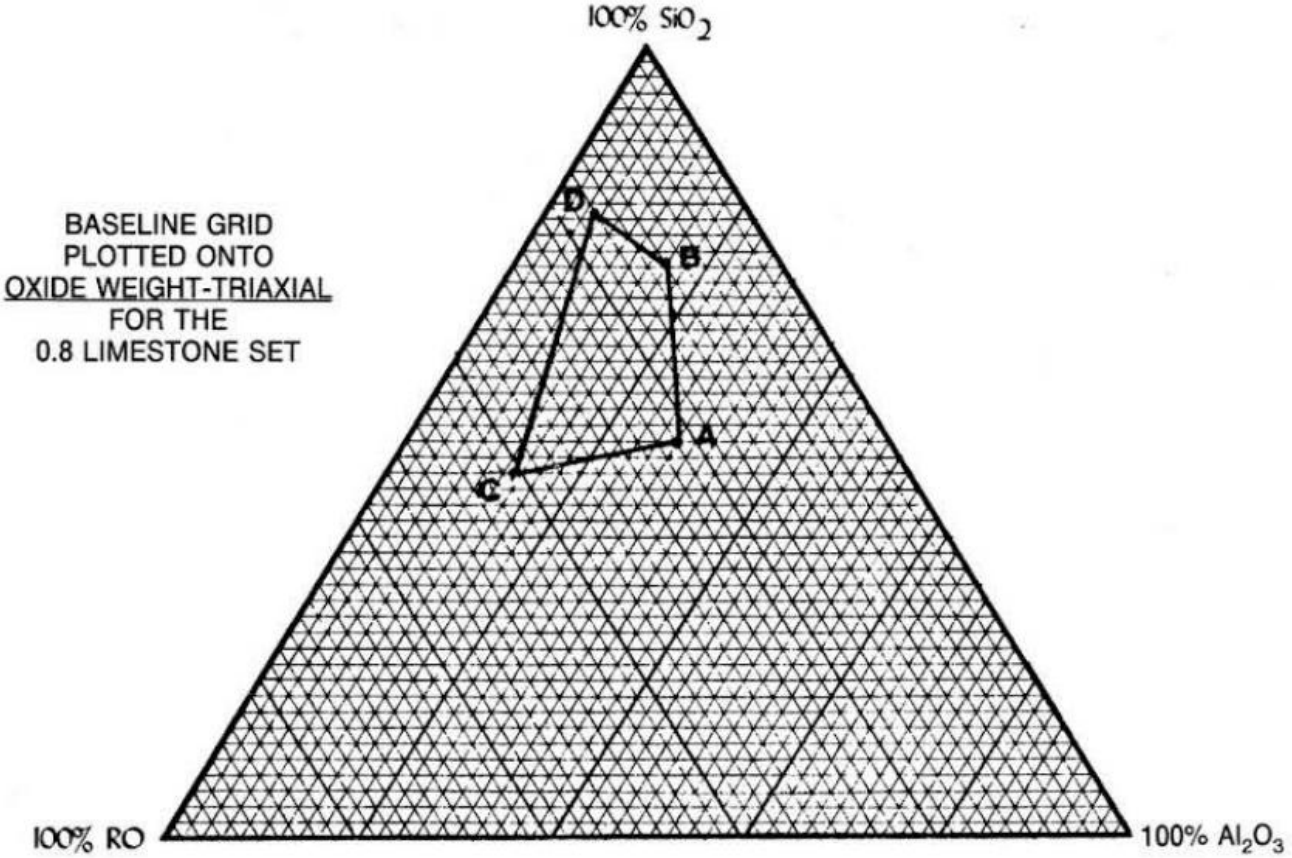
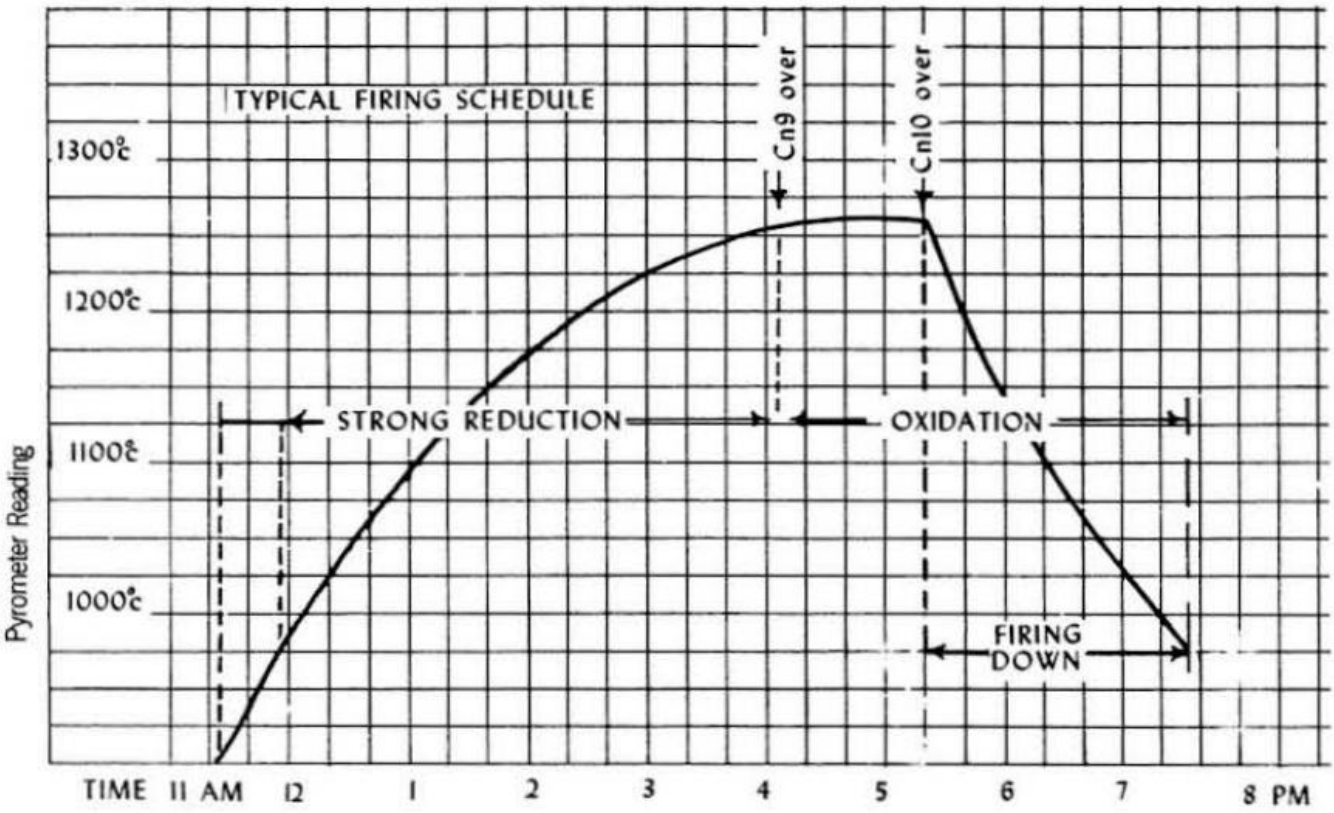


DIAGRAM 8.3



4. Firings

For the results given here, all the firings were done in a small (6 cu.ft) L.P. gas-fired kiln. The firing cycles were slowed down in the final stages, including cooling, to give more variety to the results — to give results similar to firing in a brick kiln. Quicker firing and cooling, such as can be achieved in a fibre kiln, gives less variety of results in any one set because of less time for clay/glaze interaction and crystal growth. The cone numbers reached were:

Firings 1 and 4 : Large Orton Cone 10
Firing 2 : Large Orton Cone 13
Firing 3 : Between Large Orton Cones 13 and 14.

The temperatures reached and indicated on the Results Charts are lower than the Orton Cone Tables would suggest because of the slower soaked ending to the firings.

Firings 1, 2 and 3 were in strong reduction (0.6 — 0.7 on an A.I.C. Oxy Probe) and Firing 4 was in oxidation, otherwise fired equivalent to Firing 1. The firing schedule indicates a typical profile, in this case to Large Orton Cone 10 (reduction). See Diagram 8.3.

5. Clay Body

The clay body used was Podmore's porcelain.

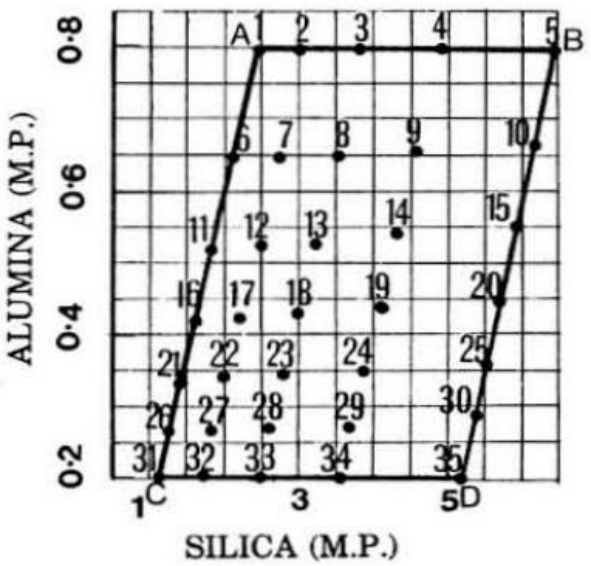
6. Glaze Materials

Analyses of the raw materials used are given in Chapter 1 under 'Guidelines for Selection of Raw Materials'. (See P. 9).

7. Glaze Numbers

The glaze numbers used for any one set are always in the same order as indicated by the diagram below:

DIAGRAM 8.4 Glaze Numbers



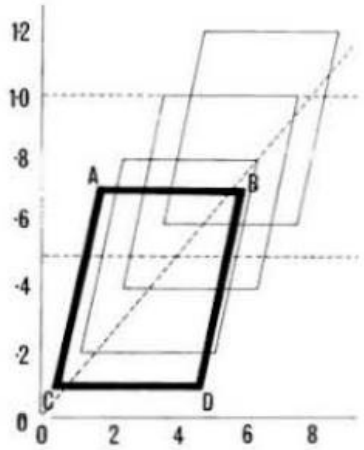
EXPERIMENT NO.2 THE 0.9 LIMESTONE SET

Corner Glazes -- The limits of the experiment:

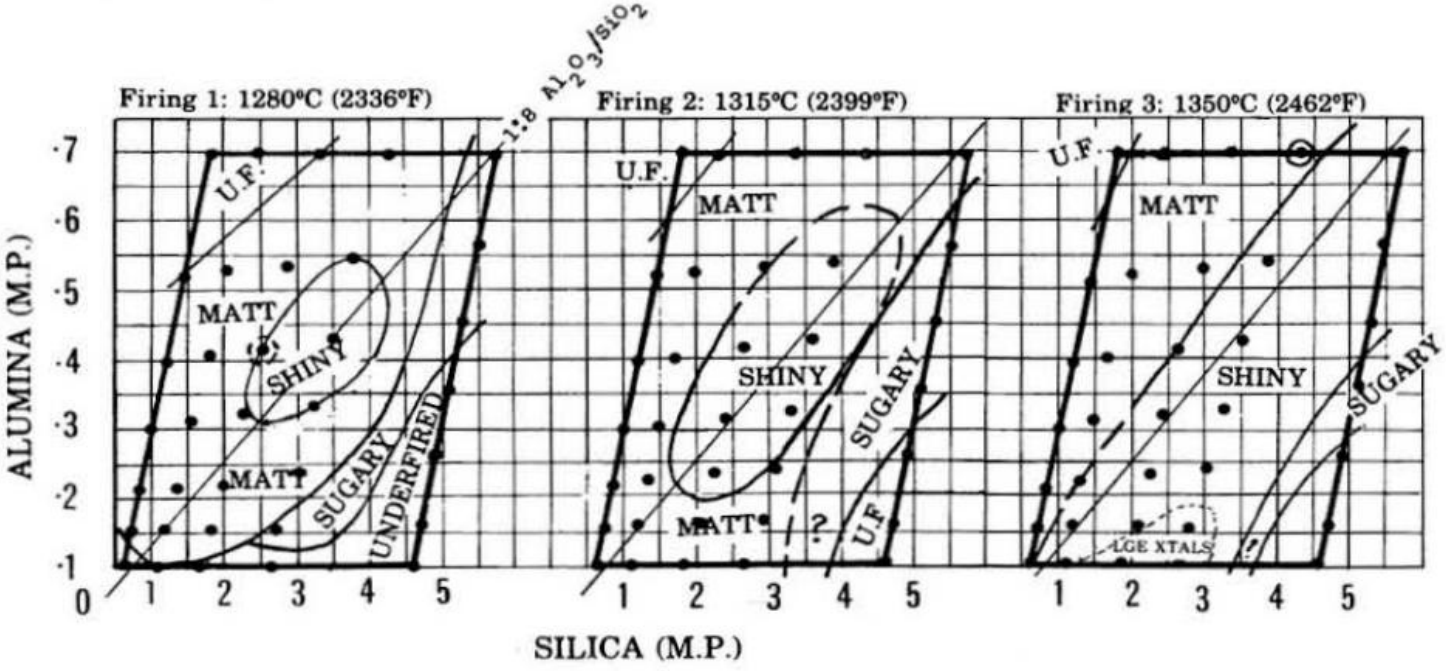
	RECIPE (%)				OXIDE WT. (%)				M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	KAOLIN	SILICA	K_2O	CaO	Al_2O_3	SiO_2	FLUXES: 0.1 K_2O 0.9 CaO Al_2O_3/SiO_2:
A	18.51	29.97	51.52	0	3.94	21.09	29.79	45.18	0.7/1.8
B	10.29	16.65	28.62	44.44	1.97	10.52	14.87	72.65	0.7/5.8
C	38.18	61.82	0	0	8.88	47.56	9.60	33.96	0.1/0.6
D	14.41	23.33	0	62.26	2.72	14.57	2.94	79.77	0.1/4.6

See 'Preliminary Comments on Experiments' (this Chapter) for experimental details including explanation of data and charts presented here.

Grid Location Diagram:



Results Charts:



0.9 LIMESTONE SET

Comments on Results

See diagrams opposite.

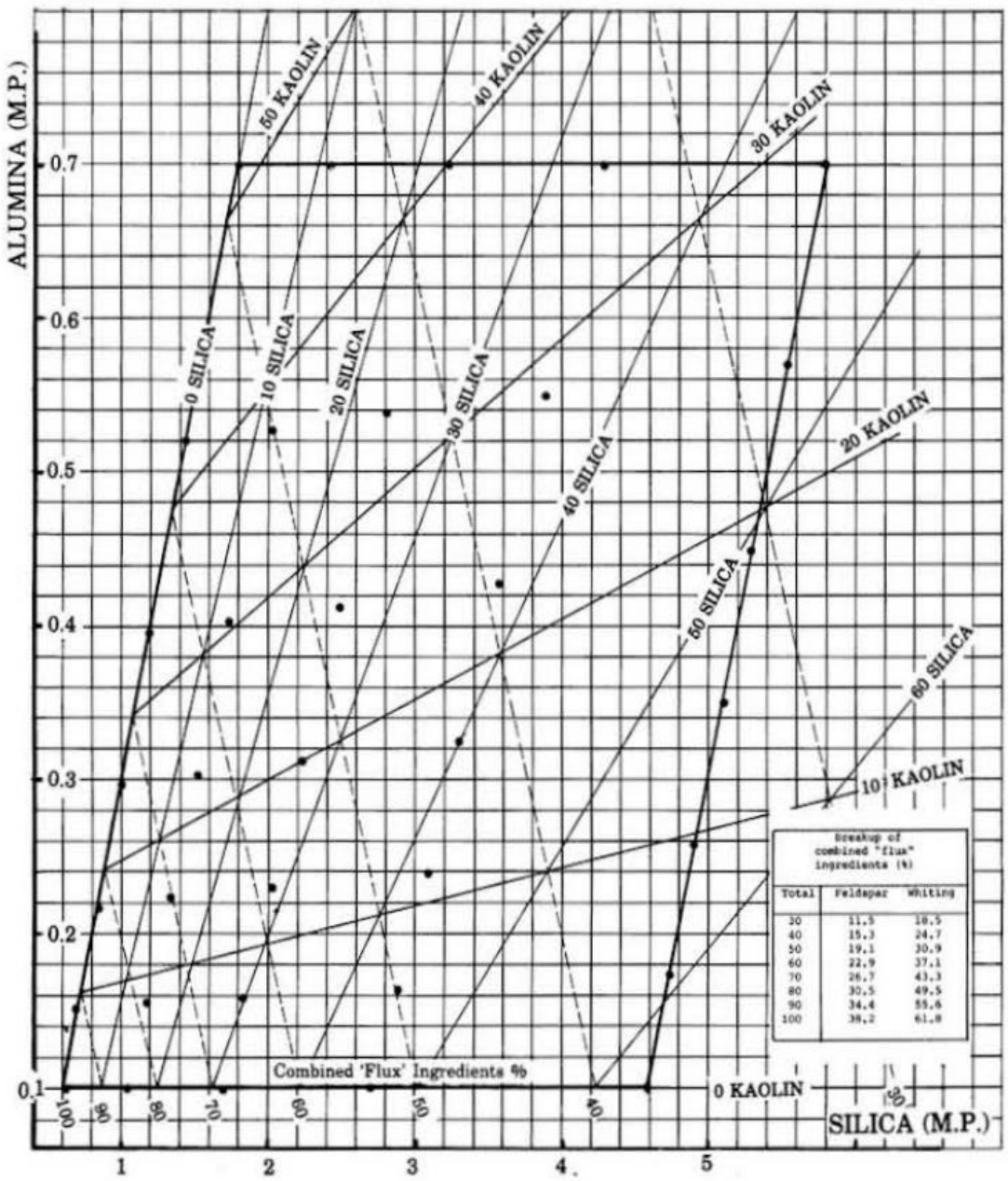
1. This set shows more underfired glazes than the others; obviously more K_2O is required to fuse many of the glazes.
2. In reduction many of the glazes along and near the kaolin baseline are discoloured by yellowish crystals, very similar to high calcium ash glazes; several of the glazes (low in alumina and silica) develop 'stringing', the interlocking rivulet patterns developed on vertical surfaces by many ash glazes. The discolouration is less noticeable in oxidation and disappears at higher temperatures, e.g. Firing 3.
3. Calcium alumina matts are evident around Glazes 6 and 11. This type of glaze is discussed more fully in Chapter 17.
4. Large crystals form in some of the low alumina glazes at high temperatures, e.g. Glazes 29, 33, 34 in Firing 3.
5. Chun-blue effect develops in Glaze 29, Firing 3, along with the crystals. The blue is aided by iron oxide in the glaze or clay body.
6. A reasonable 'orange-peel' effect is evident on Glaze 4, Firing 3.
7. As a result of the high lime content, decorations using iron oxide tend to dissolve into the glaze.
8. The high lime/low alkali content of these glazes results in less crazing than occurs in the sets with higher alkali, such as the 0.6 Limestone and 0.6 Feldspar Sets.

DATA SHEET 0.9 LIMESTONE SET

	RECIPE (%)				OXIDE WEIGHTS (%)					M.P.
GLAZE No.	K FEL	WHITING	KAOLIN	SILICA	GLAZE No.	K_2O	CaO	Al_2O_3	SiO_2	Al_2O_3/SiO_2
1	18.51	29.97	51.52	.00	1	3.94	21.09	29.79	45.18	0.7 /1.8
2	16.46	26.64	45.80	11.11	2	3.45	18.45	26.06	52.05	0.7 /2.43
3	14.40	23.31	40.07	22.22	3	2.96	15.81	22.33	58.92	0.7 /3.23
4	12.35	19.98	34.35	33.33	4	2.46	13.16	18.60	65.78	0.7 /4.30
5	10.29	16.65	28.62	44.44	5	1.97	10.52	14.87	72.65	0.7 /5.80
6	21.79	35.28	42.93	.00	6	4.76	25.50	26.43	43.31	0.52/1.45
7	19.09	30.90	38.16	11.85	7	4.10	21.93	23.04	50.94	0.53/2.04
8	16.38	26.52	33.39	23.71	8	3.43	18.35	19.65	58.57	0.54/2.82
9	13.68	22.14	28.62	35.56	9	2.76	14.77	16.27	66.21	0.55/3.91
10	10.98	17.76	23.85	47.41	10	2.10	11.20	12.88	73.84	0.57/5.54
11	25.07	40.59	34.35	.00	11	5.59	29.91	23.06	41.44	0.40/1.19
12	21.72	35.16	30.53	12.60	12	4.75	25.40	20.02	49.84	0.40/1.74
13	18.37	29.73	26.71	25.19	13	3.90	20.89	16.98	58.23	0.41/2.50
14	15.01	24.30	22.90	37.79	14	3.06	16.38	13.94	66.63	0.43/3.59
15	11.66	18.88	19.08	50.38	15	2.22	11.87	10.89	75.02	0.45/5.31
16	28.35	45.90	25.76	.00	16	6.41	34.33	19.70	39.57	0.30/0.99
17	24.35	39.42	22.90	13.34	17	5.39	28.88	17.00	48.73	0.30/1.51
18	20.35	32.94	20.04	26.68	18	4.38	23.44	14.30	57.89	0.31/2.24
19	16.35	26.47	17.17	40.01	19	3.36	17.99	11.60	67.05	0.33/3.32
20	12.35	19.99	14.31	53.35	20	2.35	12.55	8.91	76.21	0.35/5.10
21	31.62	51.20	17.17	.00	21	7.23	38.74	16.33	37.70	0.22/0.83
22	26.98	43.68	15.27	14.08	22	6.04	32.36	13.98	47.62	0.22/1.33
23	22.33	36.15	13.36	28.16	23	4.85	25.98	11.62	57.55	0.23/2.03
24	17.68	28.63	11.45	42.24	24	3.66	19.60	9.27	67.47	0.24/3.09
25	13.04	21.10	9.54	56.32	25	2.47	13.22	6.92	77.40	0.26/4.92
26	34.90	56.51	8.59	.00	26	8.06	43.15	12.97	35.83	0.15/0.71
27	29.61	47.94	7.63	14.82	27	6.69	35.84	10.96	46.52	0.16/1.17
28	24.31	39.36	6.68	29.65	28	5.33	28.52	8.95	57.21	0.16/1.85
29	19.02	30.79	5.72	44.47	29	3.96	21.21	6.94	67.90	0.16/2.89
30	13.72	22.22	4.77	59.29	30	2.60	13.90	4.93	78.58	0.17/4.75
31	38.18	61.82	.00	.00	31	8.88	47.56	9.60	33.96	0.10/0.60
32	32.24	52.20	.00	15.57	32	7.34	39.31	7.94	45.41	0.10/1.05
33	26.30	42.58	.00	31.13	33	5.80	31.07	6.27	56.87	0.10/1.70
34	20.35	32.95	.00	46.70	34	4.26	22.82	4.61	68.32	0.10/2.72
35	14.41	23.33	.00	62.26	35	2.72	14.57	2.94	79.77	0.10/4.60

RECIPE CHART

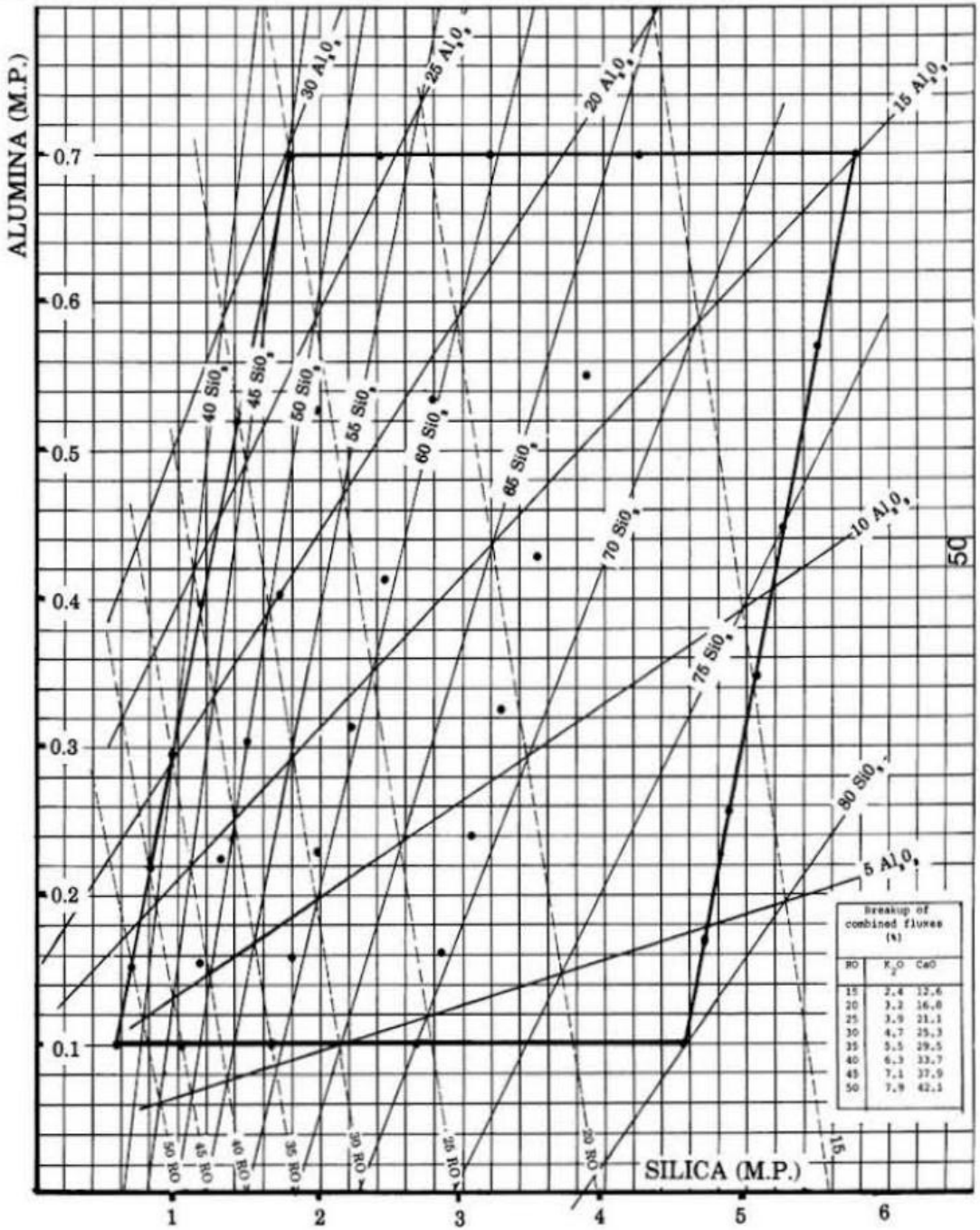
0.9 LIMESTONE SET



Breakup of combined "flux" ingredients (%)

Total	Feldspar	Whiting
30	11.5	18.5
40	15.3	24.7
50	19.1	30.9
60	22.9	37.1
70	26.7	43.3
80	30.5	49.5
90	34.4	55.6
100	38.2	61.8

OXIDE WEIGHTS CHART

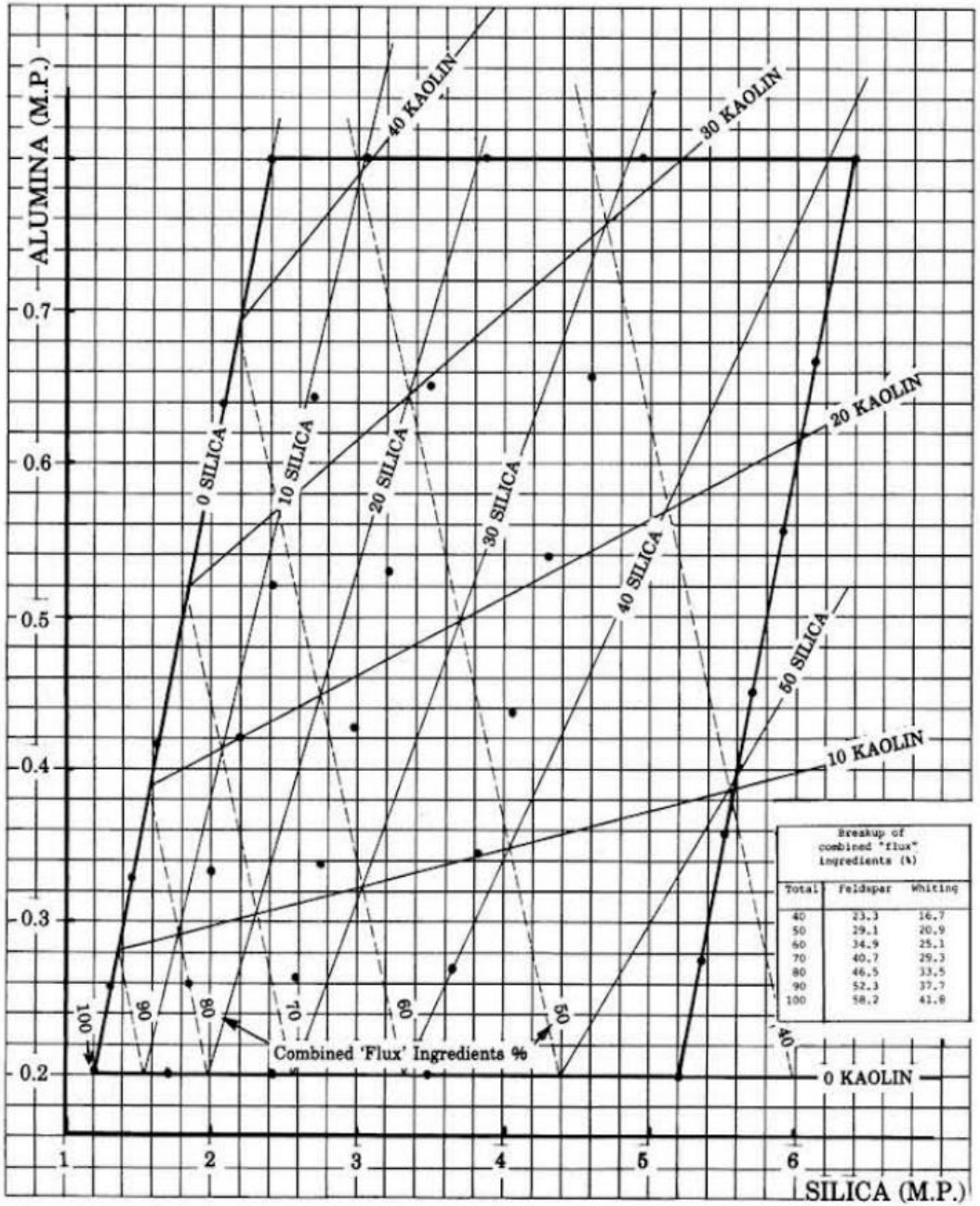


Breakup of combined fluxes (%)

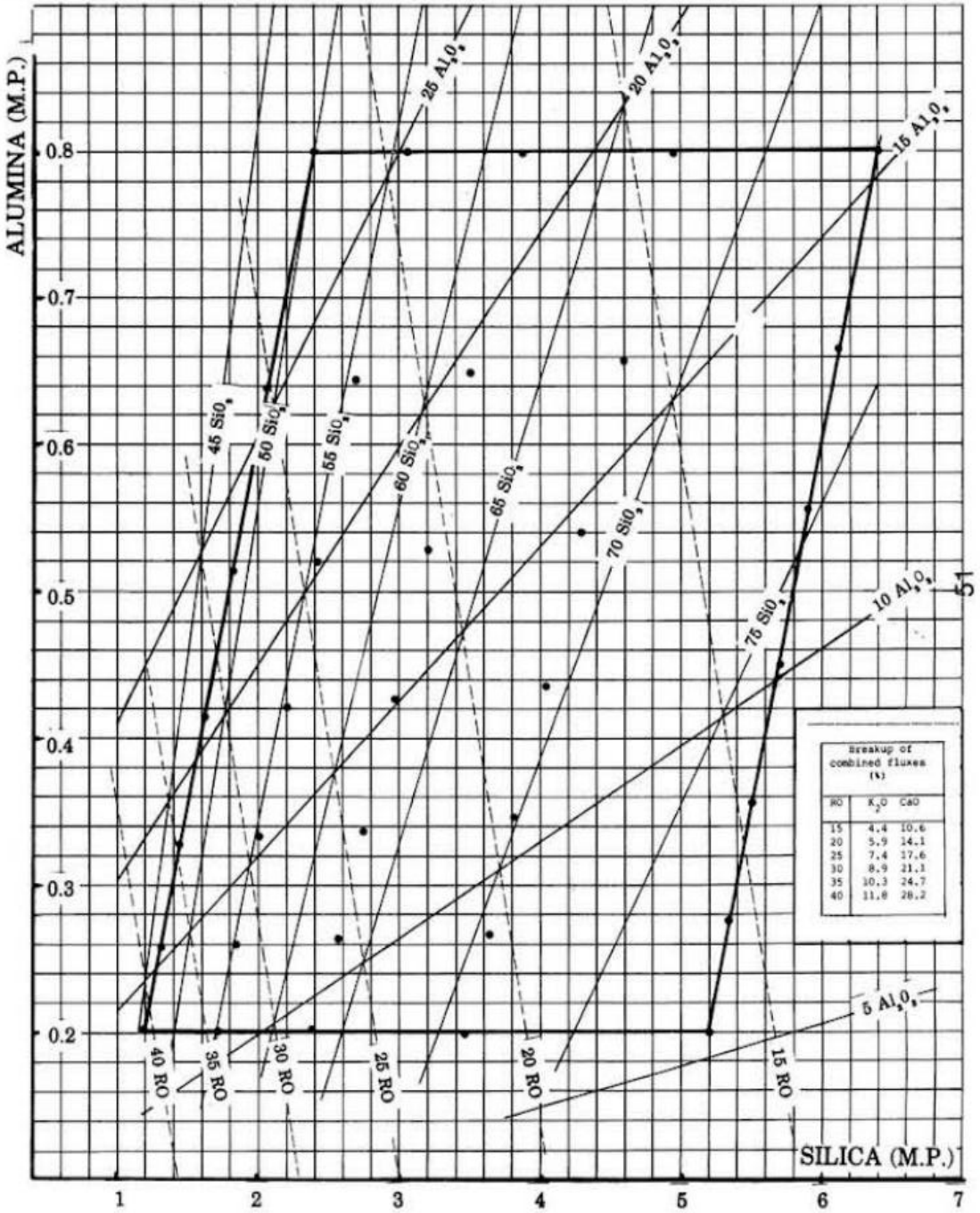
RO	K_2O	CaO
15	2.4	12.6
20	3.2	16.8
25	3.9	21.1
30	4.7	25.3
35	5.5	29.5
40	6.3	33.7
45	7.1	37.9
50	7.9	42.1

RECIPE CHART

0.8 LIMESTONE SET



OXIDE WEIGHTS CHART



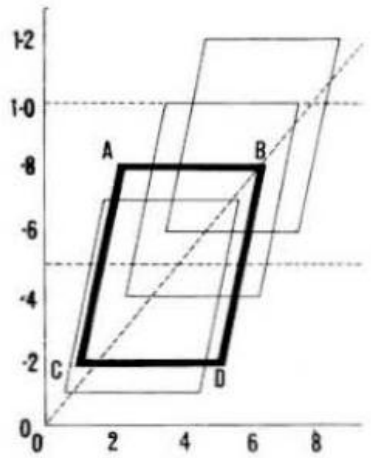
EXPERIMENT NO.3 THE 0.8 LIMESTONE SET

Corner Glazes — The limits of the experiment:

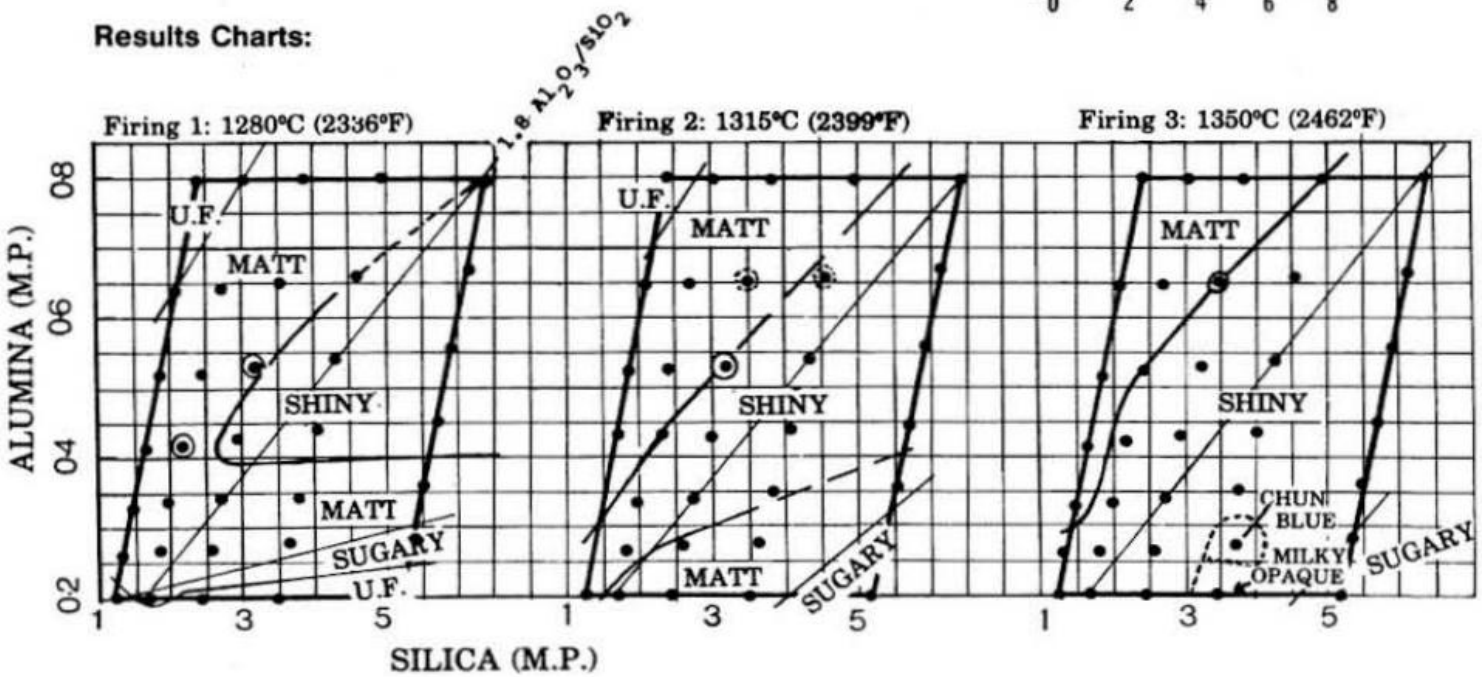
	RECIPE (%)				OXIDE WT. (%)				M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	KAOLIN	SILICA	K_2O	CaO	Al_2O_3	SiO_2	FLUXES: 0.2 K_2O 0.8 CaO
									Al_2O_3/SiO_2:
A	32.15	23.13	44.73	0	6.51	15.50	28.16	49.82	0.8/2.4
B	18.97	13.65	26.40	40.98	3.56	8.47	15.38	72.59	0.8/6.4
C	58.16	41.84	0	0	12.07	28.73	13.04	46.16	0.2/1.2
D	25.78	18.55	0	55.68	4.75	11.32	5.14	78.79	0.2/5.2

See 'Preliminary Comments on Experiments' (this Chapter) for experimental details including explanation of data and charts presented here.

Grid Location Diagram:



Results Charts:



0.8 LIMESTONE SET

Comments on Results

See diagrams opposite.

1. There are some very good alumina matt glazes, including some excellent 'orange-peel' glazes, e.g. Glaze 13 in Firings 1 and 2.

2. Barely visible granular crystals are evident around Glazes 16, 17, 21, 22, in Firing 1. The effect of these crystals combined with the orange-peel, bursting bubble effect, seems to be responsible for a beautiful textured matt or semi-matt surface in Glaze 17, Firing 1.

3. As firing temperatures are raised, the matt glazes 12 and 17 slowly clear, eventually producing clear shiny glazes; however, they both go through a stage of being matt where thin, and clear and shiny where thick.

4. In Firing 1, there is a wide zone of opaque silica matts, e.g. Glazes 24, 25, 28, 29. As the firing temperature rises, the opacity clears, sometimes producing the Chun-blue effect, e.g. Glaze 29, Firing 3. The Chun-blue can be brought on at lower temperatures if using an iron-y body, or slip, or iron oxide in the glaze. See Chapter 18 for more on Chun-blue glazes.

5. Adjacent to the Chun-blue glaze 29 in Firing 3 but closer to Corner D, lies a narrow zone of shiny milky white opaque glazes, becoming 'sugary' with more silica.

6. Stringing is evident in some low alumina low silica glazes.

7. There are matt pinks and discolouration evident along the kaolin baseline in Firing 1. The effect is not evident in oxidation. In Firing 2, the pink is confined to Glazes 6 and 11 and is not evident in Firing 3.

8. There are some strong uncrazed glazes useful for functional ware around Corner B. These glazes are discussed more in Chapter 19.

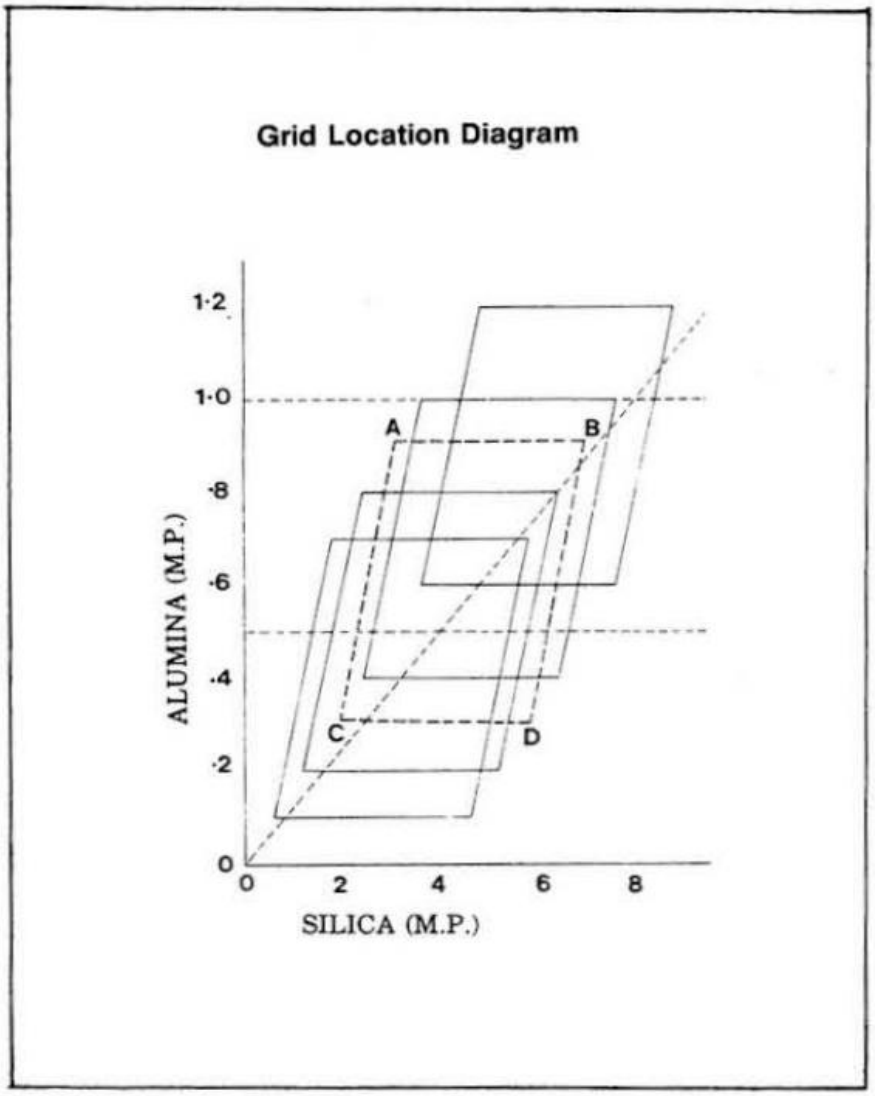
DATA SHEET 0.8 LIMESTONE SET

	RECIPE (%)				OXIDE WEIGHTS (%)				M.P.
GLAZE No.	K FEL	WHITING	KAOLIN	SILICA	GLAZE No.	K_2O	CaO	Al_2O_3	SiO_2	Al_2O_3/SiO_2
1	32.15	23.13	44.73	.00	1	6.51	15.50	28.16	49.82	0.8 /2.4
2	28.86	20.76	40.15	10.25	2	5.77	13.74	24.97	55.51	0.8 /3.06
3	25.56	18.39	35.57	20.49	3	5.04	11.99	21.77	61.21	0.8 /3.88
4	22.27	16.02	30.98	30.74	4	4.30	10.23	18.58	66.90	0.8 /4.96
5	18.97	13.65	26.40	40.98	5	3.56	8.47	15.38	72.59	0.8 /6.4
6	36.49	26.25	37.28	.00	6	7.44	17.71	25.64	49.21	0.64/2.08
7	32.39	23.30	33.46	10.86	7	6.52	15.52	22.65	55.31	0.65/2.71
8	28.30	20.36	29.64	21.72	8	5.60	13.33	19.66	61.42	0.65/3.52
9	24.20	17.41	25.82	32.57	9	4.68	11.14	16.67	67.52	0.66/4.61
10	20.11	14.47	22.00	43.43	10	3.76	8.95	13.67	73.62	0.67/6.14
11	40.82	29.37	29.82	.00	11	8.36	19.91	23.12	48.60	0.51/1.83
12	35.93	25.85	26.77	11.47	12	7.26	17.29	20.33	55.11	0.52/2.39
13	31.03	22.33	23.71	22.94	13	6.16	14.67	17.54	61.63	0.53/3.23
14	26.14	18.80	20.66	34.41	14	5.06	12.04	14.76	68.14	0.54/4.32
15	21.24	15.28	17.60	45.88	15	3.96	9.42	11.97	74.66	0.56/5.92
16	45.16	32.49	22.37	.00	16	9.29	22.12	20.60	47.99	0.41/1.63
17	39.46	28.39	20.07	12.08	17	8.01	19.06	18.02	54.92	0.42/2.21
18	33.77	24.29	17.78	24.17	18	6.72	16.01	15.43	61.84	0.43/2.98
19	28.07	20.20	15.49	36.25	19	5.44	12.95	12.85	68.77	0.44/4.07
20	22.38	16.1[illegible]	13.20	48.33	20	4.16	9.90	10.26	75.69	0.45/5.71
21	49.49	35.60	14.91	.00	21	10.22	24.32	18.08	47.38	0.33/1.46
22	43.00	30.93	13.38	12.70	22	8.75	20.83	15.70	54.72	0.33/2.02
23	36.50	26.26	11.86	25.39	23	7.29	17.35	13.32	62.05	0.34/2.77
24	30.01	21.59	10.33	38.09	24	5.82	13.86	10.94	69.39	0.35/3.85
25	23.51	16.92	8.80	50.78	25	4.35	10.37	8.55	76.72	0.36/5.52
26	53.83	38.72	7.46	.00	26	11.14	26.53	15.56	46.77	0.26/1.32
27	46.53	33.47	6.69	13.31	27	9.50	22.61	13.38	54.52	0.26/1.85
28	39.24	28.23	5.93	26.62	28	7.85	18.69	11.20	62.26	0.27/2.59
29	31.94	22.98	5.16	39.92	29	6.20	14.77	9.03	70.01	0.27/3.65
30	24.65	17.73	4.40	53.23	30	4.55	10.85	6.85	77.76	0.28/5.35
31	58.16	41.84	.00	.00	31	12.07	28.73	13.04	46.16	0.2 /1.2
32	50.07	36.02	.00	13.92	32	10.24	24.38	11.07	54.32	0.2 /1.72
33	41.97	30.20	.00	27.84	33	8.41	20.03	9.09	62.48	0.2 /2.43
34	33.88	24.37	.00	41.76	34	6.58	15.67	7.12	70.63	0.2 /3.48
35	25.78	18.55	.00	55.68	35	4.75	11.32	5.14	78.79	0.2 /5.2

DATA SHEET 0.7 LIMESTONE SET

	RECIPE (%)				OXIDE WT. (%)				M.P.
	K FEL	WHITING	KAOLIN	SILICA	K_2O	CaO	Al_2O_3	SiO_2	Al_2O_3/SiO_2
1	42.60	17.88	39.52	.00	8.33	11.56	27.01	53.10	0.9 /3.0
2	38.55	16.18	35.76	9.51	7.47	10.36	24.21	57.96	0.9 /3.69
3	34.50	14.48	32.01	19.01	6.61	9.17	21.41	62.82	0.9 /4.53
4	30.45	12.78	28.25	28.52	5.74	7.97	18.61	67.68	0.9 /5.60
5	26.40	11.08	24.49	38.02	4.88	6.77	15.81	72.54	0.9 /7.0
6	47.24	19.83	32.93	.00	9.23	12.81	24.98	52.99	0.75/2.70
7	42.39	17.79	29.80	10.02	8.20	11.38	22.31	58.11	0.75/3.37
8	37.53	15.75	26.67	20.04	7.17	9.96	19.65	63.22	0.76/4.20
9	32.68	13.72	23.54	30.06	6.15	8.53	16.98	68.34	0.77/5.29
10	27.83	11.68	20.41	40.08	5.12	7.11	14.32	73.46	0.77/6.75
11	51.88	21.77	26.35	.00	10.12	14.05	22.95	52.88	0.63/2.46
12	46.22	19.40	23.84	10.53	8.93	12.40	20.42	58.25	0.63/3.10
13	40.57	17.03	21.34	21.07	7.74	10.75	17.88	63.63	0.64/3.92
14	34.91	14.65	18.83	31.60	6.55	9.10	15.35	69.00	0.65/5.01
15	29.26	12.28	16.33	42.13	5.36	7.44	12.82	74.37	0.66/6.52
16	56.52	23.72	19.76	.00	11.02	15.30	20.92	52.77	0.53/2.25
17	50.06	21.01	17.88	11.05	9.67	13.42	18.52	58.40	0.53/2.88
18	43.60	18.30	16.00	22.09	8.31	11.54	16.12	64.03	0.54/3.68
19	37.14	15.59	14.12	33.14	6.96	9.66	13.72	69.66	0.55/4.77
20	30.69	12.88	12.25	44.19	5.61	7.78	11.33	75.29	0.56/6.32
21	61.16	25.67	13.17	.00	11.92	16.54	18.88	52.66	0.44/2.08
22	53.90	22.62	11.92	11.56	10.40	14.43	16.62	58.55	0.44/2.68
23	46.64	19.57	10.67	23.12	8.88	12.33	14.36	64.43	0.45/3.47
24	39.38	16.53	9.42	34.68	7.36	10.22	12.09	70.32	0.45/4.56
25	32.11	13.48	8.16	46.24	5.85	8.12	9.83	76.20	0.46/6.13
26	65.80	27.61	6.59	.00	12.81	17.79	16.85	52.55	0.36/1.93
27	57.74	24.23	5.96	12.07	11.13	15.45	14.72	58.69	0.37/2.51
28	49.67	20.85	5.33	24.15	9.45	13.12	12.59	64.83	0.37/3.29
29	41.61	17.46	4.71	36.22	7.77	10.79	10.46	70.97	0.37/4.37
30	33.54	14.08	4.08	48.30	6.09	8.45	8.34	77.12	0.38/5.96
31	70.44	29.56	.00	.00	13.71	19.03	14.82	52.44	0.30/1.80
32	61.57	25.84	.00	12.59	11.87	16.47	12.83	58.84	0.30/2.37
33	52.71	22.12	.00	25.18	10.02	13.91	10.83	65.24	0.30/3.13
34	43.84	18.40	.00	37.76	8.18	11.35	8.84	71.63	0.30/4.19
35	34.97	14.68	.00	50.35	6.33	8.79	6.84	78.03	0.30/5.80

0.7 LIMESTONE SET



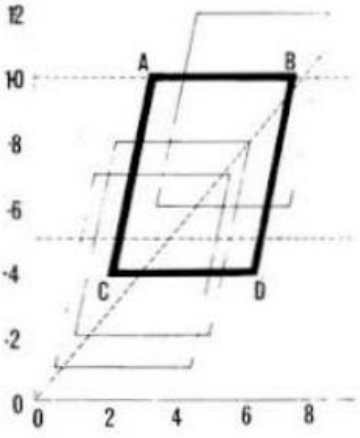
EXPERIMENT NO.4 THE 0.6 LIMESTONE SET

Corner Glazes — The limits of the experiment:

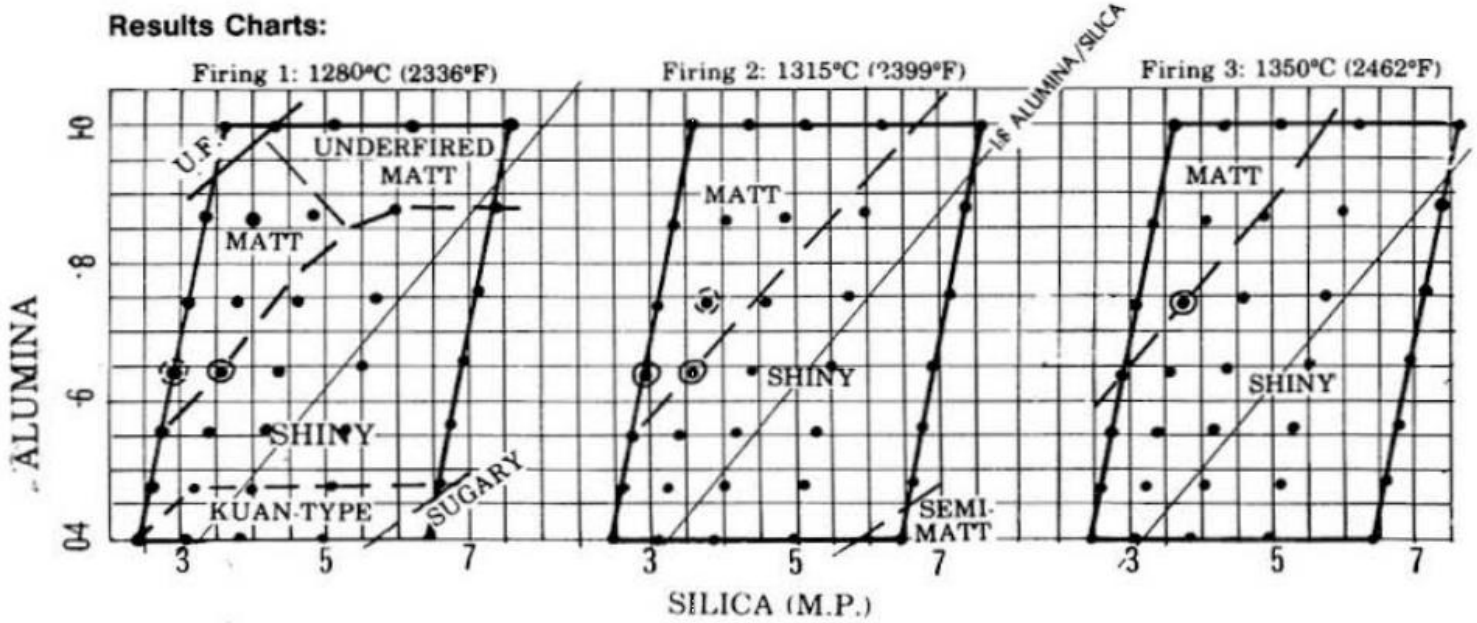
	RECIPE (%)				OXIDE WT. (%)				M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	KAOLIN	SILICA	K_2O	CaO	Al_2O_3	SiO_2	FLUXES: 0.4 K_2O 0.6 CaO Al_2O_3/SiO_2:
A	50.88	13.73	35.39	0	9.68	8.64	26.15	55.53	1.0/3.6
B	32.84	8.86	22.84	35.46	5.99	5.34	16.17	72.5	1.0/7.6
C	78.75	21.25	0	0	14.71	13.13	15.90	56.26	0.4/2.4
D	42.56	11.48	0	45.96	7.59	6.78	8.20	77.43	0.4/6.4

See 'Preliminary Comments on Experiments' (this Chapter) for experimental details including explanation of data and charts presented here.

Grid Location Diagram



Results Charts:



0.6 LIMESTONE SET

Comments on Results
See diagrams opposite.

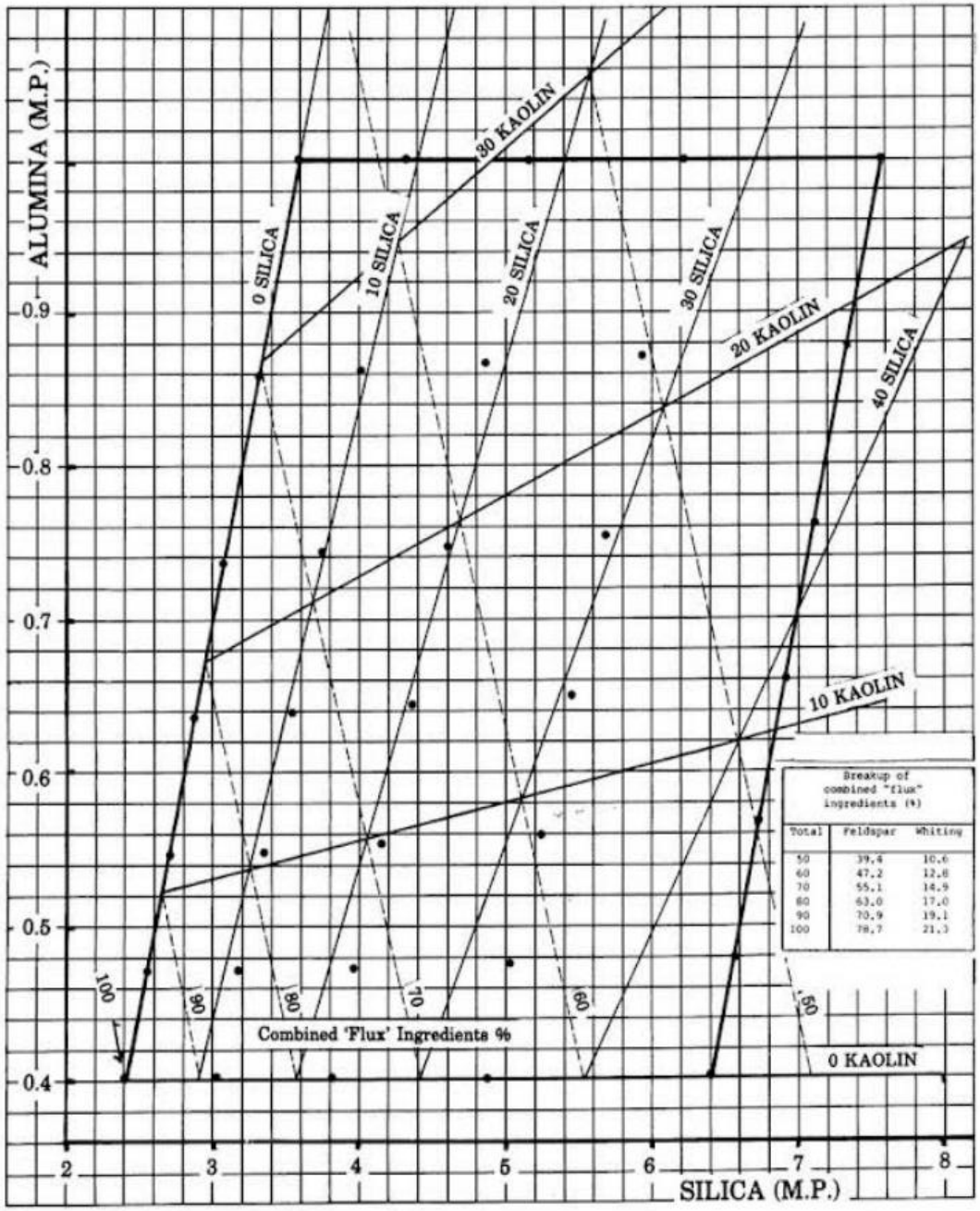
1. The nature of these glazes is beginning to become dominated by the presence of feldspar. Virtually all glazes are crazed on the Podmore's porcelain. Many of the glazes give Kuan-type effects, depending on temperature.
2. There are some superb semi-matt opaque white glazes along the top row at high temperature, e.g. Glazes 2 and 3 in Firing 3.
3. Most of the glazes are quite stiff, but in Firings 2 and 3, the glazes around Corner C become runny, glassy and highly crazed.
4. Matt pinks occur along the kaolin baseline, e.g. Glazes 6, 11, 16 in Firings 1 and 2 (reduction).
5. There are some good 'orange-peel' glazes, e.g. Glazes 16, 17 in Firings 1 and 2, and Glaze 12 in Firing 3.

DATA SHEET — 0.6 LIMESTONE SET

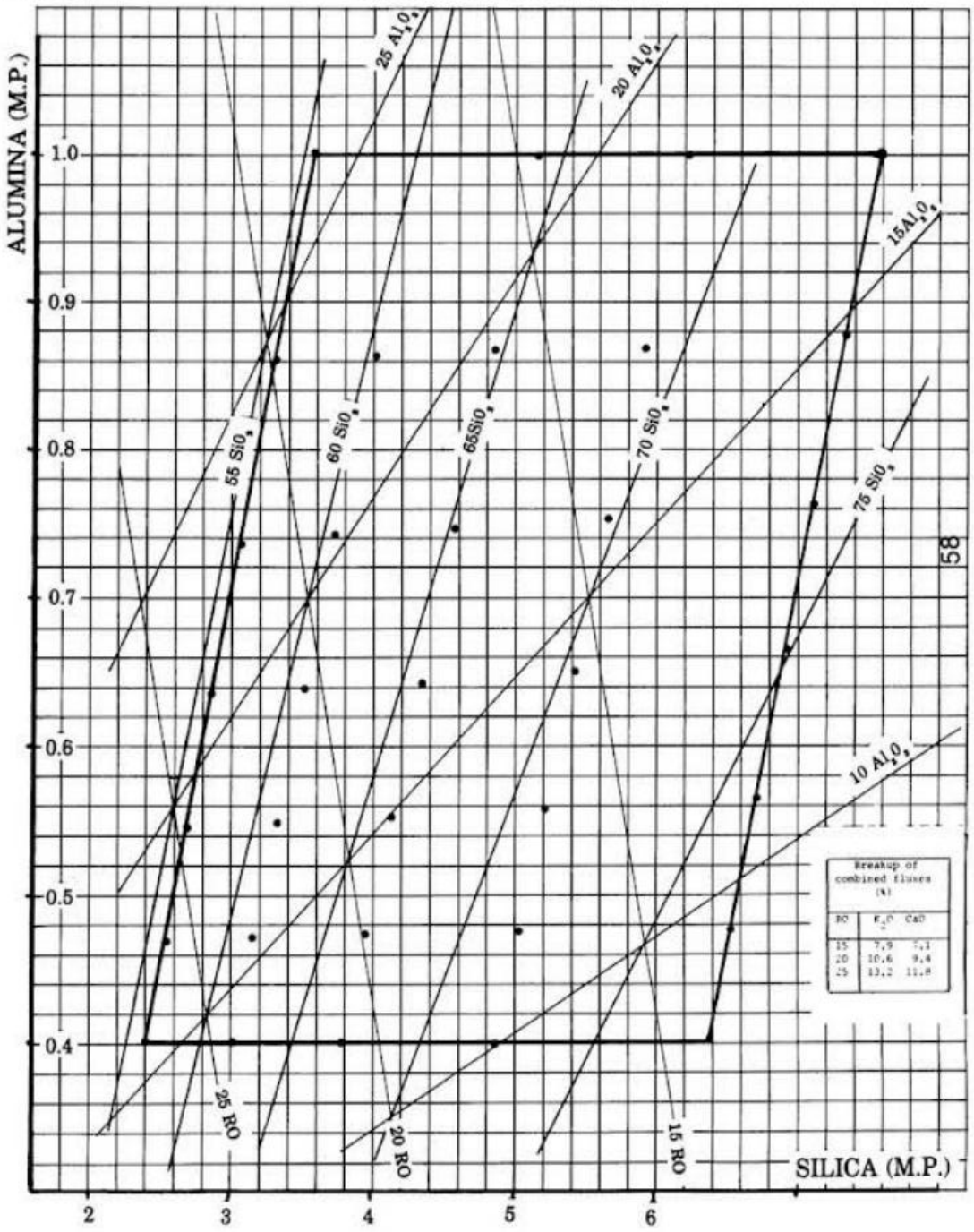
	RECIPE (%)				OXIDE WEIGHTS (%)					M.P.
GLAZE No.	K FEL	WHITING	KAOLIN	SILICA	GLAZE No.	K_2O	CaO	Al_2O_3	SiO_2	Al_2O_3/SiO_2
1	50.88	13.73	35.39	.00	1	9.68	8.64	26.15	55.53	1.0 /3.60
2	46.37	12.51	32.25	8.87	2	8.76	7.82	23.66	59.77	1.0 /4.31
3	41.86	11.30	29.12	17.73	3	7.84	6.99	21.16	64.02	1.0 /5.17
4	37.35	10.08	25.98	26.60	4	6.91	6.17	18.67	68.26	1.0 /6.24
5	32.84	8.86	22.84	35.46	5	5.99	5.34	16.17	72.50	1.0 /7.60
6	55.53	14.98	29.49	.00	6	10.52	9.39	24.44	55.65	0.86/3.32
7	50.26	13.56	26.88	9.30	7	9.45	8.44	22.04	60.07	0.86/4.01
8	44.99	12.14	24.26	18.61	8	8.39	7.48	19.64	64.49	0.87/4.86
9	39.73	10.72	21.65	27.91	9	7.32	6.53	17.24	68.90	0.87/5.94
10	34.46	9.30	19.03	37.21	10	6.26	5.58	14.84	73.32	0.88/7.35
11	60.17	16.24	23.59	.00	11	11.36	10.14	22.73	55.77	0.74/3.08
12	54.15	14.61	21.50	9.74	12	10.15	9.06	20.43	60.37	0.74/3.75
13	48.13	12.99	19.41	19.48	13	8.94	7.98	18.12	64.96	0.75/4.59
14	42.10	11.36	17.32	29.22	14	7.73	6.90	15.82	69.55	0.75/5.68
15	36.08	9.73	15.23	38.96	15	6.52	5.82	13.51	74.14	0.76/7.13
16	64.82	17.49	17.70	.00	16	12.20	10.89	21.03	55.90	0.64/2.87
17	58.04	15.66	16.13	10.18	17	10.84	9.68	18.82	60.66	0.64/3.53
18	51.26	13.83	14.56	20.36	18	9.49	8.47	16.61	65.43	0.64/4.36
19	44.48	12.00	12.99	30.53	19	8.14	7.27	14.40	70.20	0.65/5.45
20	37.70	10.17	11.42	40.71	20	6.79	6.06	12.19	74.97	0.66/6.92
21	69.46	18.74	11.80	.00	21	13.03	11.63	19.32	56.02	0.55/2.69
22	61.93	16.71	10.75	10.62	22	11.54	10.30	17.20	60.96	0.55/3.33
23	54.39	14.68	9.71	21.23	23	10.05	8.97	15.09	65.90	0.55/4.15
24	46.86	12.64	8.66	31.85	24	8.55	7.63	12.97	70.84	0.56/5.24
25	39.32	10.61	7.61	42.46	25	7.06	6.30	10.86	75.79	0.57/6.73
26	74.11	20.00	5.90	.00	26	13.87	12.38	17.61	56.14	0.47/2.54
27	65.81	17.76	5.38	11.05	27	12.23	10.92	15.59	61.26	0.47/3.16
28	57.52	15.52	4.85	22.11	28	10.60	9.46	13.57	66.37	0.47/3.97
29	49.23	13.28	4.33	33.16	29	8.96	8.00	11.55	71.49	0.48/5.05
30	40.94	11.04	3.81	44.21	30	7.32	6.54	9.53	76.61	0.48/6.56
31	78.75	21.25	.00	.00	31	14.71	13.13	15.90	56.26	0.40/2.40
32	69.70	18.81	.00	11.49	32	12.93	11.54	13.98	61.55	0.40/3.01
33	60.66	16.37	.00	22.98	33	11.15	9.96	12.05	66.85	0.40/3.80
34	51.61	13.92	.00	34.47	34	9.37	8.37	10.13	72.14	0.40/4.87
35	42.56	11.48	.00	45.96	35	7.59	6.78	8.20	77.43	0.40/6.40

RECIPE CHART

0.6 LIMESTONE SET

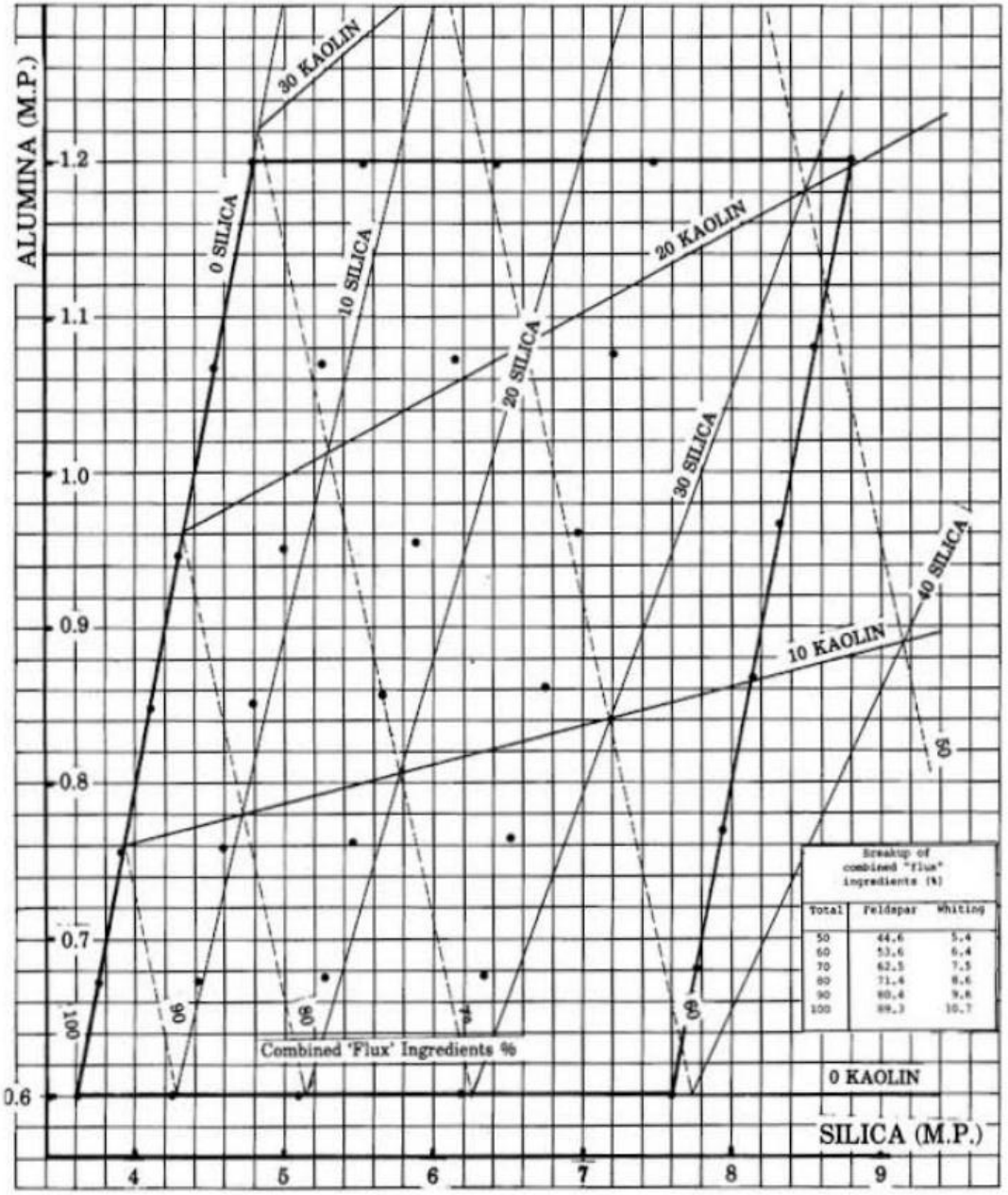


OXIDE WEIGHTS CHART

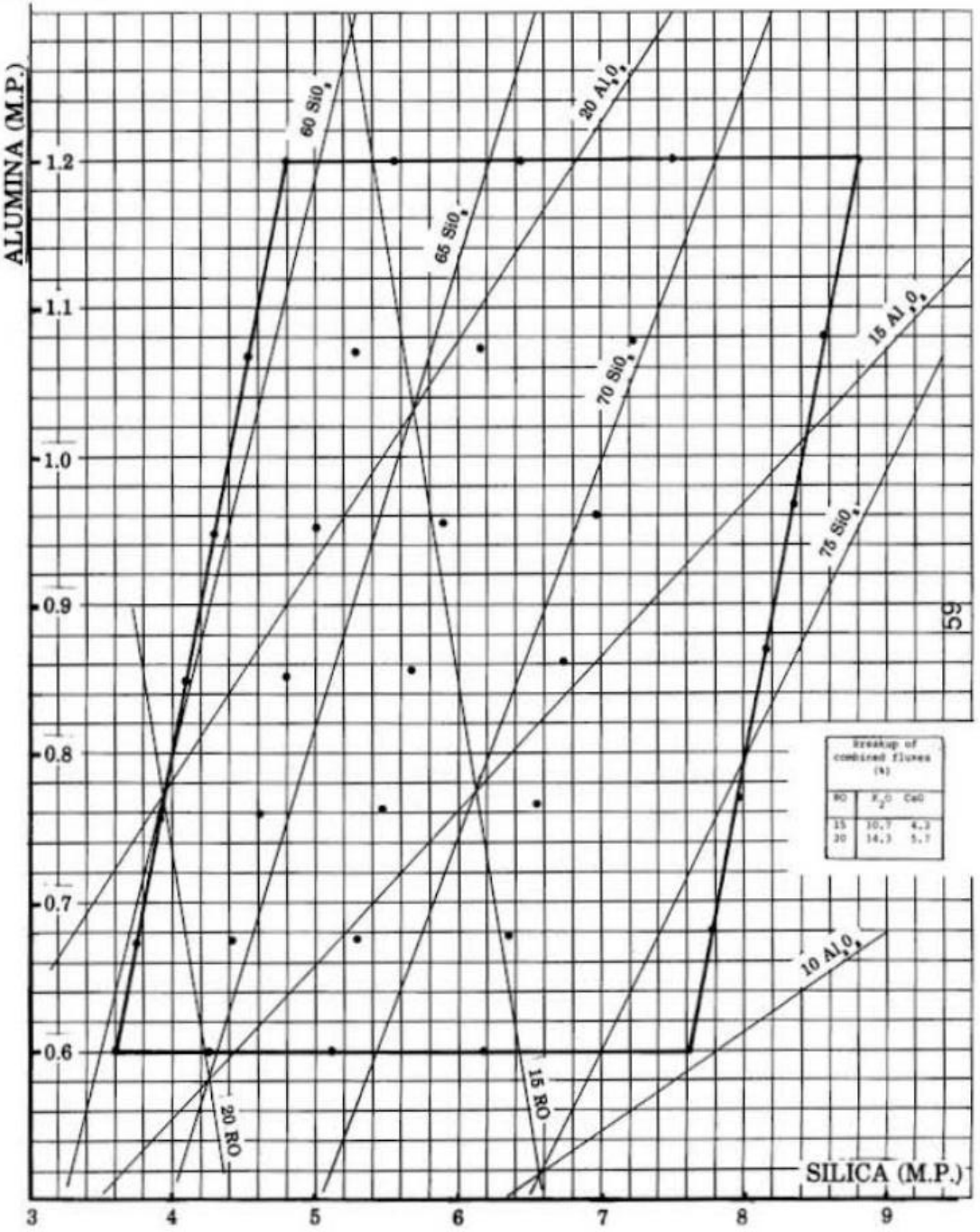


RECIPE CHART

0.6 FELDSPAR SET



OXIDE WEIGHTS CHART



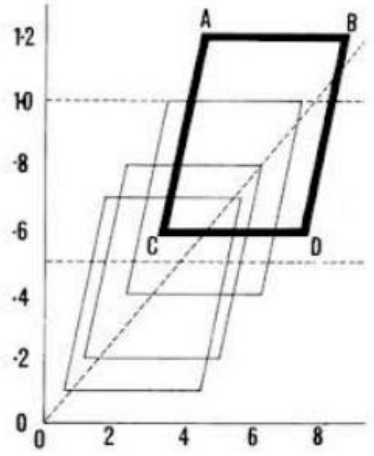
EXPERIMENT NO.5 THE 0.6 FELDSPAR SET

Corner Glazes — The limits of the experiment:

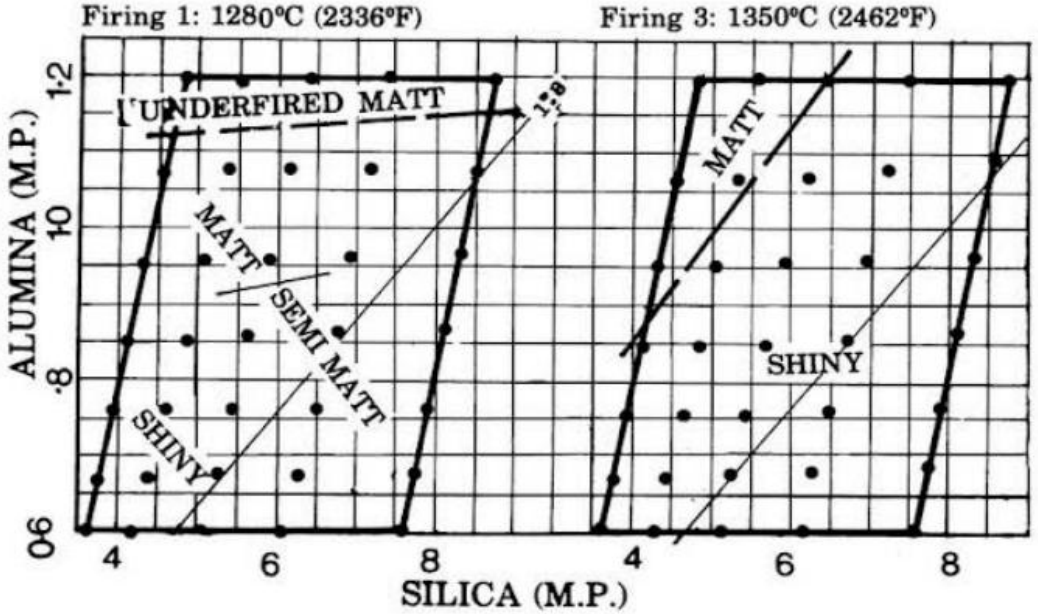
	RECIPE (%)				OXIDE WT. (%)				M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	KAOLIN	SILICA	K_2O	CaO	Al_2O_3	SiO_2	FLUXES: 0.6 K_2O 0.4 CaO Al_2O_3/SiO_2:
A	63.14	7.57	29.29	0	11.55	4.58	24.97	58.90	1.2/4.8
B	43.41	5.21	20.13	31.25	7.75	3.07	16.75	72.43	1.2/8.8
C	89.29	10.71	0	0	15.87	6.29	17.15	60.69	0.6/3.6
D	54.35	6.52	0	39.13	9.48	3.76	10.24	76.52	0.6/7.6

See 'Preliminary Comments on Experiments' (this Chapter) for experimental details including explanation of data and charts presented here.

Grid Location Diagram:



Results Charts:



0.6 FELDSPAR SET

Comments on results
See diagrams opposite.

1. The effect of the feldspar is now quite overpowering to the point where little change is to be observed from one glaze to the next; in fact, this set could be quite adequately sampled with 12 glazes, eliminating every second glaze (in the 35) horizontally and vertically. All the glazes craze on Podmore's porcelain.
2. There is some suggestion of the matt pink effect on Glazes 11, 16 in Firing 1.
3. As with the 0.6 Limestone Set, most of the glazes are quite stiff, but in Firings 2 and 3, the glazes around Corner C become runny, glassy and highly crazed.
4. Iron oxide in reduction produces some excellent rust, or 'kaki' colours, especially in the high alumina glazes, at high temperature. At lower temperature, the effect is more a dark crystalline 'tessha'.

DATA SHEET — 0.6 FELDSPAR SET

	RECIPE (%)				OXIDE WEIGHTS (%)				M.P.
GLAZE No.	K FEL	WHITING	KAOLIN	SILICA	GLAZE No.	K_2O	CaO	Al_2O_3	SiO_2	Al_2O_3/SiO_2
1	63.14	7.57	29.29	.00	1	11.55	4.58	24.97	58.90	1.20/4.80
2	58.21	6.98	27.00	7.81	2	10.60	4.20	22.92	62.28	1.20/5.55
3	53.28	6.39	24.71	15.63	3	9.65	3.83	20.86	65.67	1.20/6.43
4	48.34	5.80	22.42	23.44	4	8.70	3.45	18.81	69.05	1.20/7.49
5	43.41	5.21	20.13	31.25	5	7.75	3.07	16.75	72.43	1.20/8.80
6	67.50	8.09	24.41	.00	6	12.27	4.87	23.67	59.20	1.07/4.54
7	61.93	7.43	22.50	8.14	7	11.21	4.45	21.67	62.68	1.07/5.27
8	56.37	6.76	20.59	16.28	8	10.15	4.03	19.67	66.16	1.07/6.15
9	50.80	6.09	18.68	24.42	9	9.10	3.61	17.67	69.63	1.08/7.22
10	45.23	5.43	16.78	32.56	10	8.04	3.19	15.67	73.11	1.08/8.56
11	71.86	8.62	19.53	.00	11	12.99	5.15	22.36	59.50	0.95/4.30
12	65.66	7.87	18.00	8.47	12	11.82	4.69	20.42	63.07	0.95/5.03
13	59.46	7.13	16.47	16.94	13	10.66	4.23	18.47	66.65	0.96/5.90
14	53.26	6.39	14.95	25.41	14	9.49	3.76	16.53	70.22	0.96/6.98
15	47.06	5.65	13.42	33.88	15	8.33	3.30	14.58	73.79	0.97/8.33
16	76.22	9.14	14.65	.00	16	13.71	5.44	21.06	59.80	0.85/4.10
17	69.38	8.32	13.50	8.80	17	12.44	4.93	19.17	63.47	0.85/4.81
18	62.55	7.50	12.36	17.60	18	11.16	4.43	17.28	67.14	0.86/5.67
19	55.71	6.68	11.21	26.39	19	9.89	3.92	15.39	70.81	0.86/6.75
20	48.88	5.87	10.07	35.19	20	8.62	3.42	13.50	74.48	0.87/8.13
21	80.57	9.66	9.76	.00	21	14.43	5.72	19.76	60.09	0.76/3.91
22	73.11	8.77	9.00	9.13	22	13.05	5.17	17.92	63.86	0.76/4.61
23	65.64	7.87	8.24	18.25	23	11.67	4.63	16.08	67.63	0.76/5.47
24	58.17	6.98	7.47	27.38	24	10.29	4.08	14.25	71.39	0.77/6.55
25	50.70	6.08	6.71	36.50	25	8.90	3.53	12.41	75.16	0.77/7.94
26	84.93	10.19	4.88	.00	26	15.15	6.01	18.45	60.39	0.67/3.75
27	76.83	9.22	4.50	9.45	27	13.66	5.42	16.67	64.25	0.68/4.43
28	68.73	8.24	4.12	18.91	28	12.17	4.83	14.89	68.12	0.68/5.28
29	60.63	7.27	3.74	28.36	29	10.68	4.24	13.11	71.98	0.68/6.36
30	52.53	6.30	3.36	37.82	30	9.19	3.65	11.33	75.84	0.68/7.77
31	89.29	10.71	.00	.00	31	15.87	6.29	17.15	60.69	0.60/3.60
32	80.56	9.66	.00	9.78	32	14.27	5.66	15.42	64.65	0.60/4.27
33	71.82	8.62	.00	19.57	33	12.68	5.03	13.70	68.61	0.60/5.11
34	63.09	7.57	.00	29.35	34	11.08	4.39	11.97	72.56	0.60/6.18
35	54.35	6.52	.00	39.13	35	9.48	3.76	10.24	76.52	0.60/7.60

9 MAGNESIUM GLAZES

In stoneware glazes, magnesia (MgO) is often used as a matting agent, giving some excellent opaque matt glazes. It is also very useful in helping to reduce crazing, though the amount used is usually much less than the 0.5 M.P. used in the Magnesium Set here. Interesting colour responses are achieved with cobalt and iron oxide pigments. In glazes fairly low in alumina and containing about 0.2 M.P. MgO, a pleasant speckle of pyroxene crystals is fairly easily produced. In an iron glaze, this gives the 'teadust' effect.

Data is given for 3 sets, but only the Magnesium Set is studied in full here:

Magnesium Set:	**Intermediate Sets:**	
0.2 K_2O	0.2 K_2O	0.2 K_2O
0.3 CaO	0.5 CaO	0.7 CaO
0.5 MgO	0.3 MgO	0.1 MgO

SOURCES OF MAGNESIA

Note: See also comments on talc, dolomite, and magnesium carbonate in Chapter 1 under 'Raw Materials'.

a. Magnesium carbonate

This is usually provided by pottery suppliers in two forms, 'heavy' and 'light'. Heavy magnesium carbonate is usually ground magnesite, mostly $MgCO_3$ with some noticeable impurities such as calcium and silica. Pure $MgCO_3$ can be obtained. Light magnesium carbonate has the formula $3MgCO_3.Mg(OH)_2.3H_2O$, is usually very pure, and weight for weight provides about 7 to 8% less MgO than does pure $MgCO_3$. However, this difference is undetectable in most glazes; the differences that are observed are most likely due to impurities in the magnesite, and crawling caused by the light material. A glaze made up with light magnesium carbonate needs more water than one using 'heavy', takes up more volume in the bucket and shrinks more in drying causing crawling.

b. Talc ($3MgO.4SiO_2.H_2O$)

The mineral talc is the main ingredient in the rock steatite, or soapstone, and is a very useful source of magnesia in glazes.

c. Dolomite ($CaCO_3.MgCO_3$)

Variable in composition, but nevertheless it should be tried as it produces good magnesia glazes with subtle differences from the other magnesia sources.

d. Basic Igneous Rocks

(See Cardew and McMeekin references and also Chapter 26 for more information on rocks and minerals).
Igneous rocks low in silica such as basalt, dolerite, gabbro etc. usually contain significant amounts of magnesia in the form of the minerals olivine, augite and others. However they usually also contain significant amounts of iron oxide so this source of magnesia is of significance mainly in iron glazes such as tenmoku, teadust etc.

e. Some Wood Ashes

Most wood ashes contain a little MgO, but in Cardew's *Pioneer Pottery* on page 54, you will find an analysis of Eucalyptus microcorys (Tallowwood) ash in which the principal components are:

52.15% CaO, 25.58% MgO, 8.98% SiO_2, 6.84% Na_2O, 2.41% K_2O.

With an analysis like this, it would probably perform not unlike dolomite, though I have not been able to obtain any to try so far. Tallowwood is a fairly common native tree in south-east Queensland and northern New South Wales bordering on rainforest. See Chapter 25 for more analyses of wood ashes.

With both the basic igneous rocks and wood ash, you will not be able to use either the Seger Formula or the Oxide Percentage approach unless you can get an analysis. However, this should not stop you using an empirical approach such as was outlined in Chapter 4.

DATA SHEET — MAGNESIUM SET

MAGNESIUM SET (Using Light $MgCO_3$) RECIPE (%)

GLAZE No.	K FEL.	WHITING	Lt.$MgCO_3$	KAOLIN	SILICA
1	32.56	8.78	13.35	45.30	.00
2	29.20	7.88	11.97	40.63	10.32
3	25.84	6.97	10.60	35.95	20.65
4	22.48	6.07	9.22	31.28	30.97
5	19.12	5.16	7.84	26.60	41.29
6	37.06	9.99	15.19	37.75	.00
7	32.86	8.86	13.47	33.85	10.95
8	28.66	7.73	11.75	29.96	21.89
9	24.47	6.60	10.03	26.06	32.84
10	20.27	5.47	8.31	22.17	43.78
11	41.55	11.21	17.04	30.20	.00
12	36.52	9.85	14.97	27.08	11.57
13	31.49	8.50	12.91	23.97	23.14
14	26.46	7.14	10.85	20.85	34.71
15	21.43	5.78	8.79	17.73	46.28
16	46.05	12.42	18.88	22.65	.00
17	40.18	10.84	16.48	20.31	12.19
18	34.31	9.26	14.07	17.98	24.39
19	28.45	7.68	11.67	15.64	36.58
20	22.58	6.10	9.26	13.30	48.77
21	50.54	13.63	20.72	15.10	.00
22	43.84	11.83	17.98	13.54	12.82
23	37.14	10.02	15.23	11.98	25.63
24	30.44	8.21	12.48	10.43	38.45
25	23.73	6.41	9.73	8.87	51.26
26	55.04	14.85	22.57	7.55	.00
27	47.50	12.81	19.48	6.77	13.44
28	39.96	10.78	16.39	5.99	26.88
29	32.42	8.75	13.30	5.21	40.32
30	24.89	6.72	10.21	4.43	53.76
31	59.53	16.06	24.41	.00	.00
32	51.16	13.80	20.98	.00	14.06
33	42.79	11.55	17.55	.00	28.13
34	34.41	9.29	14.11	.00	42.19
35	26.04	7.03	10.68	.00	56.25

MAGNESIUM SETS OXIDE WEIGHTS (%)

GLAZE No.	K_2O	CaO	MgO	Al_2O_3	SiO_2	M.P.
1	6.70	5.98	7.16	28.95	51.22	
2	5.93	5.29	6.34	25.62	56.84	
3	5.16	4.60	5.51	22.29	62.46	
4	4.38	3.91	4.69	18.95	68.07	
5	3.61	3.22	3.86	15.62	73.69	
6	7.70	6.88	8.23	26.42	50.79	
7	6.73	6.01	7.19	23.28	56.79	
8	5.76	5.14	6.16	20.15	62.80	
9	4.79	4.27	5.12	17.02	68.80	
10	3.82	3.41	4.08	13.89	74.81	
11	8.70	7.77	9.30	23.88	50.35	
12	7.53	6.73	8.05	20.95	56.75	
13	6.36	5.68	6.80	18.02	63.14	
14	5.19	4.64	5.55	15.09	69.53	
15	4.02	3.59	4.30	12.16	75.92	
16	9.71	8.67	10.37	21.35	49.92	
17	8.34	7.44	8.91	18.62	56.70	
18	6.97	6.22	7.45	15.89	63.48	
19	5.60	5.00	5.98	13.16	70.26	
20	4.23	3.78	4.52	10.43	77.04	
21	10.71	9.56	11.44	18.81	49.49	
22	9.14	8.16	9.77	16.28	56.65	
23	7.57	6.76	8.09	13.76	63.82	
24	6.00	5.36	6.42	11.23	70.99	
25	4.44	3.96	4.74	8.70	78.16	
26	11.71	10.46	12.51	16.28	49.05	
27	9.94	8.88	10.62	13.95	56.61	
28	8.18	7.30	8.74	11.62	64.16	
29	6.41	5.72	6.85	9.30	71.72	
30	4.64	4.15	4.96	6.97	79.27	
31	12.71	11.35	13.58	13.74	48.62	
32	10.75	9.60	11.48	11.62	56.56	
33	8.78	7.84	9.38	9.49	64.51	
34	6.82	6.09	7.28	7.37	72.45	
35	4.85	4.33	5.18	5.24	80.39	

Alumina/Silica (M.P.) Figures same as for the 0.8 Limestone Set

MAGNESIUM SET — ALTERNATIVE RECIPES (USING HEAVY $MgCO_3$)

The Magnesium Set is made up using light magnesium carbonate, and the recipes are calculated accordingly.

This alternative set of recipes is given for comparison using heavy magnesium carbonate. The two intermediate sets are calculated using the 'heavy' form.

	K FEL	WHITING	H.MgCO3	KAOLIN	SILICA
1	32.90	8.88	12.46	45.77	.00
2	29.48	7.96	11.17	41.02	10.39
3	26.07	7.04	9.87	36.27	20.77
4	22.65	6.11	8.58	31.51	31.16
5	19.23	5.19	7.28	26.76	41.54
6	37.53	10.13	14.21	38.14	.00
7	33.25	8.97	12.59	34.18	11.02
8	28.96	7.82	10.97	30.22	22.03
9	24.68	6.66	9.35	26.26	33.05
10	20.40	5.51	7.72	22.30	44.07
11	42.15	11.38	15.96	30.51	.00
12	37.01	9.99	14.01	27.35	11.65
13	31.86	8.60	12.07	24.18	23.30
14	26.72	7.21	10.12	21.01	34.95
15	21.57	5.82	8.17	17.84	46.60
16	46.78	12.63	17.72	22.89	.00
17	40.77	11.00	15.44	20.51	12.28
18	34.76	9.38	13.16	18.13	24.56
19	28.75	7.76	10.89	15.76	36.84
20	22.75	6.14	8.61	13.38	49.13
21	51.41	13.87	19.47	15.26	.00
22	44.53	12.02	16.86	13.67	12.91
23	37.66	10.16	14.26	12.09	25.83
24	30.79	8.31	11.66	10.50	38.74
25	23.92	6.45	9.05	8.92	51.65
26	56.03	15.12	21.22	7.63	.00
27	48.30	13.03	18.29	6.84	13.55
28	40.56	10.94	15.36	6.04	27.09
29	32.82	8.85	12.43	5.25	40.64
30	25.09	6.77	9.50	4.46	54.18
31	60.66	16.37	22.97	.00	.00
32	52.06	14.05	19.71	.00	14.18
33	43.46	11.73	16.46	.00	28.36
34	34.86	9.40	13.20	.00	42.53
35	26.26	7.08	9.94	.00	56.71

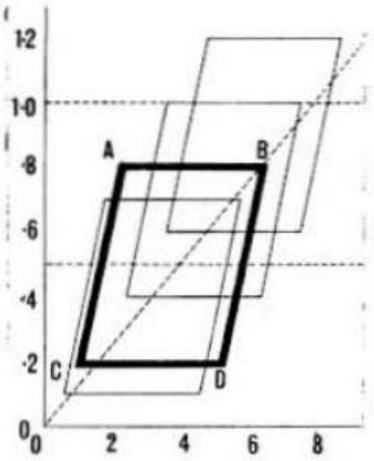
EXPERIMENT NO.6 THE MAGNESIUM SET

Corner Glazes – The limits of the experiment:

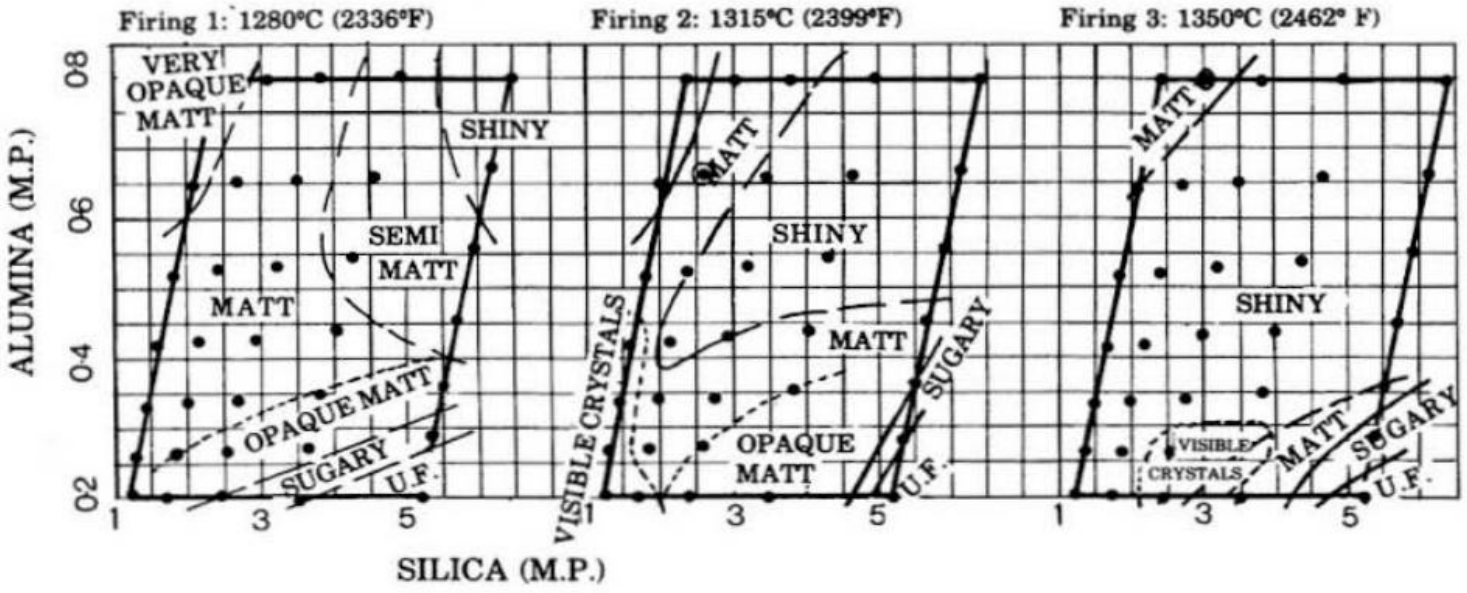
	RECIPE (%)					OXIDE WT. (%)					M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	LIGHT MAG CARB.	KAOLIN	SILICA	K_2O	CaO	MgO	Al_2O_3	SiO_2	FLUXES: 0.2 K_2O 0.3 CaO 0.5 MgO
											Al_2O_3/SiO_2:
A	32.56	8.78	13.35	45.30	0	6.70	5.98	7.16	28.95	51.22	0.8/2.4
B	19.12	5.16	7.84	26.60	41.29	3.61	3.22	3.86	15.62	73.69	0.8/6.4
C	59.53	16.06	24.41	0	0	12.71	11.35	13.58	13.74	48.62	0.2/1.2
D	26.04	7.03	10.68	0	56.25	4.85	4.33	5.18	5.24	80.39	0.2/5.2

See 'Preliminary Comments on Experiments' (Chapter 8) for experimental details including explanation of data and charts presented here.

Grid Location Diagram:



Results Charts:



MAGNESIUM SET

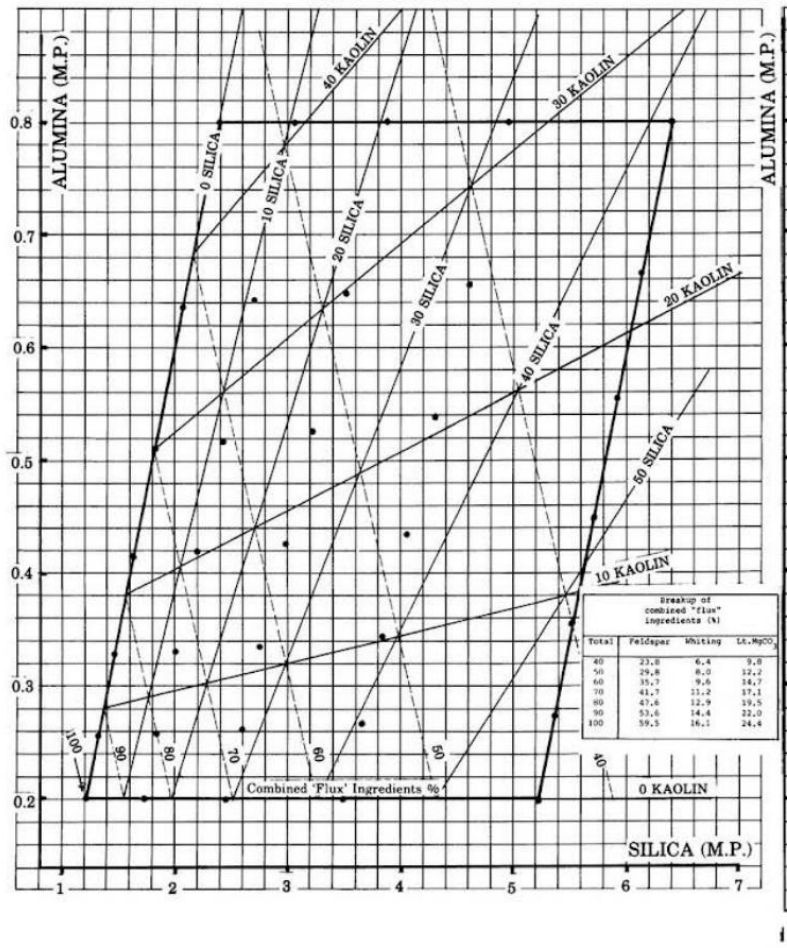
Comments on Results
See diagrams opposite.

1. There is a preponderance of excellent matt glazes at lower temperatures, e.g. white very opaque alumina matts with Glazes 1 and 6 in Firings 1 and 2, plus the more usual semi-opaque alumina matts with a little more silica. There are some interesting matt pinks, e.g. Glazes 11, 16, 21, 26, 31 in Firing 1. Also some speckled crystalline matts occur along the kaolin baseline at lower temperatures (e.g. Glazes 16, 21 in Firings 1 and 2), and along or close to the silica baseline at higher firing temperatures (e.g. Glaze 32 in Firing 2, and Glazes 28, 29, 33 in Firing 3). Like the 0.8 Limestone Set, there are a number of opaque silica matt glazes. These clear with higher temperatures to give speckled and/or Chun-blue effects (the speckling along the silica baseline mentioned above). The speckling can be achieved at lower temperatures if less MgO is used (e.g. 0.2 — 0.3 M.P.), and the effect can be used in a wide range of glazes with colouring oxides.
2. The effect with cobalt oxide is interesting: the normal cobalt blue is obtained in Corner B (high alumina and silica), but purples are obtained in the low alumina glazes, e.g. the bottom 2 or 3 rows; a soft pleasant blue is obtained in the high alumina opaque matt glazes, e.g. Glazes 1 and 6 in Firings 1 and 2. The cobalt colours hold in oxidation or reduction.
3. Iron oxide gives dull browns when applied heavily, but in the glazes that give the cobalt purples, a light application of iron gives golden yellows, the colour being much the same in oxidation of reduction. Both the iron yellow and the cobalt purple are associated with microscopic crystal growth and colouration.
4. Crazing is less than in most of the other sets, indicating the role MgO can play in reducing crazing.
5. At high temperatures, e.g. Firing 3, magnesium alumina matts tend to become clear and shiny. Contrast this with the barium alumina matts.
6. This set of glazes will vary considerably depending on the source of MgO, because of chemical and physical differences, including impurities. The results given here are using light magnesium carbonate, which is usually very pure, but which can cause crawling, especially in the high-clay glazes (along the top rows); however, unlike the crawling caused by colloidal zinc oxide, this crawling can heal over as the glaze matures, initially producing a 'lizard skin' texture, and eventually healing over almost completely, leaving a few random pinholes in the matt surface, a pleasant 'pigskin' effect.
7. The 'oatmeal' glaze is a magnesia alumina matt, usually using dolomite as the source of MgO, applied to a stoneware body (rather than porcelain), and usually having less MgO than CaO, e.g. 0.3:0.5 M.P.

RECIPE CHART

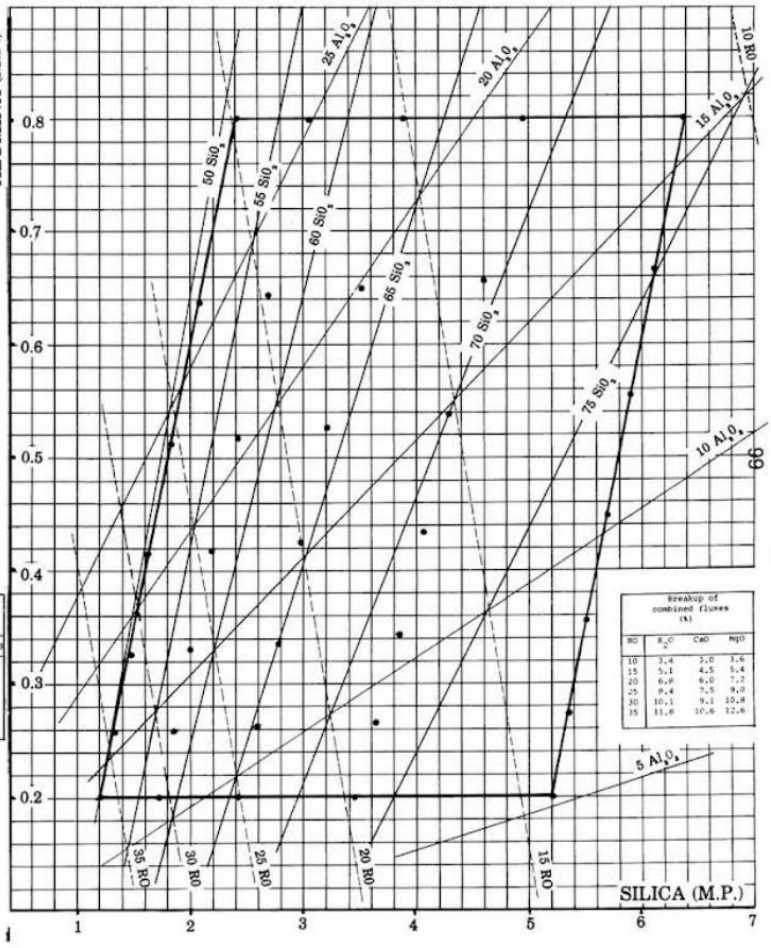
MAGNESIUM SET

OXIDE WEIGHTS CHART



Breakup of combined "flux" Ingredients (%)

Total	Feldspar	Whiting	Lt.$MgCO_3$
40	23.8	6.4	9.8
50	29.8	8.0	12.2
60	35.7	9.6	14.7
70	41.7	11.2	17.1
80	47.6	12.9	19.5
90	53.6	14.4	22.0
100	59.5	16.1	24.4



Breakup of combined fluxes (%)

RO	K_2O	CaO	MgO
10	3.4	3.0	3.6
15	5.1	4.5	5.4
20	6.8	6.0	7.2
25	8.4	7.5	9.0
30	10.1	9.1	10.8
35	11.8	10.6	12.6

MAGNESIUM GLAZES -- INTERMEDIATE SETS

0.3 Magnesium Set (0.2 K_2O, 0.5 CaO, 0.3 MgO)

RECIPES (%)

	K FEL	WHITING	H.MgCO3	KAOLIN	SILICA
1	32.59	14.66	7.41	45.35	.00
2	29.23	13.15	6.65	40.67	10.33
3	25.86	11.63	5.88	35.98	20.66
4	22.50	10.12	5.12	31.30	30.98
5	19.13	8.60	4.35	26.61	41.31
6	37.10	16.69	8.43	37.79	.00
7	32.89	14.80	7.48	33.89	10.95
8	28.69	12.90	6.52	29.98	21.90
9	24.49	11.01	5.57	26.08	32.86
10	20.29	9.12	4.61	22.18	43.81
11	41.60	18.71	9.46	30.23	.00
12	36.56	16.45	8.31	27.11	11.58
13	31.52	14.18	7.17	23.99	23.15
14	26.48	11.91	6.02	20.86	34.73
15	21.44	9.64	4.87	17.74	46.30
16	46.11	20.74	10.48	22.68	.00
17	40.23	18.10	9.14	20.33	12.20
18	34.35	15.45	7.81	17.99	24.40
19	28.47	12.81	6.47	15.65	36.60
20	22.60	10.16	5.14	13.31	48.80
21	50.62	22.77	11.50	15.12	.00
22	43.90	19.75	9.98	13.56	12.82
23	37.18	16.72	8.45	11.99	25.65
24	30.47	13.70	6.92	10.43	38.47
25	23.75	10.68	5.40	8.87	51.30
26	55.12	24.79	12.53	7.56	.00
27	47.57	21.40	10.81	6.78	13.45
28	40.01	18.00	9.09	6.00	26.90
29	32.46	14.60	7.38	5.22	40.35
30	24.91	11.20	5.66	4.44	53.79
31	59.63	26.82	13.55	.00	.00
32	51.24	23.05	11.64	.00	14.07
33	42.85	19.27	9.74	.00	28.15
34	34.45	15.50	7.83	.00	42.22
35	26.06	11.72	5.92	.00	56.29

OXIDE WTS (%)

	K_2O	CaO	MgO	Al_2O_3	SiO_2
1	6.62	9.85	4.25	28.63	50.65
2	5.86	8.72	3.76	25.35	56.30
3	5.11	7.60	3.28	22.08	61.95
4	4.35	6.47	2.79	18.80	67.59
5	3.59	5.34	2.30	15.52	73.24
6	7.59	11.29	4.87	26.10	50.14
7	6.64	9.88	4.26	23.03	56.19
8	5.69	8.47	3.65	19.95	62.23
9	4.74	7.06	3.04	16.88	68.28
10	3.79	5.64	2.43	13.80	74.32
11	8.56	12.74	5.49	23.57	49.63
12	7.42	11.04	4.76	20.70	56.08
13	6.28	9.34	4.03	17.83	62.52
14	5.14	7.64	3.29	14.95	68.96
15	4.00	5.95	2.56	12.08	75.41
16	9.54	14.18	6.12	21.04	49.13
17	8.20	12.20	5.26	18.37	55.97
18	6.87	10.22	4.40	15.70	62.81
19	5.53	8.23	3.55	13.03	69.65
20	4.20	6.25	2.69	10.36	76.49
21	10.51	15.62	6.74	18.51	48.62
22	8.98	13.36	5.76	16.04	55.86
23	7.46	11.09	4.78	13.58	63.10
24	5.93	8.82	3.80	11.11	70.33
25	4.40	6.55	2.82	8.64	77.57
26	11.48	17.07	7.36	15.98	48.11
27	9.76	14.51	6.26	13.72	55.75
28	8.04	11.96	5.15	11.45	63.38
29	6.32	9.41	4.05	9.19	71.02
30	4.61	6.86	2.95	6.92	78.66
31	12.45	18.51	7.98	13.45	47.60
32	10.54	15.67	6.76	11.39	55.64
33	8.63	12.84	5.53	9.33	63.67
34	6.72	10.00	4.31	7.26	71.71
35	4.81	7.16	3.08	5.20	79.74

0.1 Magnesium Set (0.2 K_2O, 0.7 CaO, 0.1 MgO)

RECIPES (%)

	K FEL	WHITING	H.MgCO3	KAOLIN	SILICA
1	32.29	20.33	2.45	44.93	.00
2	28.97	18.24	2.20	40.32	10.27
3	25.66	16.16	1.95	35.70	20.55
4	22.34	14.07	1.69	31.09	30.82
5	19.02	11.98	1.44	26.47	41.09
6	36.68	23.10	2.78	37.44	.00
7	32.55	20.50	2.47	33.60	10.89
8	28.42	17.90	2.15	29.75	21.78
9	24.29	15.30	1.84	25.90	32.67
10	20.16	12.70	1.53	22.06	43.56
11	41.07	25.86	3.11	29.95	.00
12	36.13	22.75	2.74	26.88	11.51
13	31.19	19.64	2.36	23.80	23.01
14	26.25	16.53	1.99	20.72	34.52
15	21.30	13.42	1.61	17.65	46.02
16	45.47	28.63	3.45	22.47	.00
17	39.71	25.00	3.01	20.16	12.12
18	33.96	21.38	2.57	17.85	24.24
19	28.20	17.76	2.14	15.54	36.36
20	22.45	14.14	1.70	13.24	48.49
21	49.86	31.39	3.78	14.98	.00
22	43.29	27.26	3.28	13.44	12.74
23	36.72	23.12	2.78	11.90	25.48
24	30.15	18.99	2.28	10.36	38.21
25	23.59	14.85	1.79	8.82	50.95
26	54.25	34.16	4.11	7.49	.00
27	46.87	29.51	3.55	6.72	13.35
28	39.49	24.86	2.99	5.95	26.71
29	32.11	20.22	2.43	5.18	40.06
30	24.73	15.57	1.87	4.41	53.42
31	58.64	36.92	4.44	.00	.00
32	50.45	31.76	3.82	.00	13.97
33	42.26	26.61	3.20	.00	27.94
34	34.06	21.45	2.58	.00	41.91
25	25.87	16.29	1.96	.00	55.88

OXIDE WTS (%)

	K_2O	CaO	MgO	Al_2O_3	SiO_2
1	6.55	13.64	1.40	28.31	50.10
2	5.81	12.09	1.24	25.09	55.78
3	5.06	10.54	1.08	21.87	61.45
4	4.32	8.98	.92	18.65	67.13
5	3.57	7.43	.76	15.43	72.80
6	7.49	15.60	1.60	25.79	49.52
7	6.56	13.66	1.40	22.77	55.60
8	5.63	11.72	1.20	19.75	61.69
9	4.70	9.79	1.00	16.74	67.77
10	3.77	7.85	.80	13.72	73.85
11	8.43	17.56	1.80	23.27	48.94
12	7.32	15.23	1.56	20.45	55.43
13	6.20	12.91	1.33	17.64	61.92
14	5.09	10.59	1.09	14.82	68.41
15	3.97	8.27	.85	12.01	74.90
16	9.37	19.52	2.01	20.75	48.37
17	8.07	16.81	1.73	18.13	55.26
18	6.77	14.10	1.45	15.52	62.16
19	5.47	11.39	1.17	12.91	69.06
20	4.17	8.69	.89	10.30	75.96
21	10.31	21.47	2.21	18.22	47.79
22	8.83	18.38	1.89	15.81	55.09
23	7.34	15.29	1.57	13.40	62.40
24	5.86	12.20	1.25	10.99	69.70
25	4.37	9.10	.93	8.58	77.01
26	11.25	23.43	2.41	15.70	47.21
27	9.58	19.95	2.05	13.49	54.92
28	7.91	16.48	1.69	11.29	62.63
29	6.24	13.00	1.33	9.08	70.35
30	4.57	9.52	.98	6.87	78.06
31	12.19	25.39	2.61	13.18	46.63
32	10.34	21.53	2.21	11.18	54.75
33	8.48	17.67	1.82	9.17	62.87
34	6.63	13.80	1.42	7.17	70.99
35	4.77	9.94	1.02	5.16	79.11

Alumina/Silica (M.P.) Figures same as for 0.8 Limestone Set

10 ZINC GLAZES

Zinc came into prominence as a glaze component around the turn of the century as a major flux in the Bristol glaze, which quickly became popular as an alternative to lead glazes when the health hazards associated with lead became known. A typical formula for a Bristol glaze fired under oxidation to Cone 6 or 7 is as follows:

0.35 KNaO
0.35 CaO 0.55 Al_2O_3 3.30 SiO_2
0.30 ZnO

By adjusting the proportions of the above oxides, fairly low melting temperatures can be obtained. For example, the following glaze gives a glossy glaze below Cone 3 (1160°C.). It lies within a 'eutectic' area for this system of oxides. (See Chapter 13 on Eutectics.) Both formulae from Parmelee:

0.4 KNaO
0.3 CaO 0.6 Al_2O_3 3.55 SiO_2
0.3 ZnO

Modern glaze technology has developed safe low temperature glazes that have replaced the Bristol glaze. Zinc oxide is substantially or completely removed from glazes fired in reduction above 950°C by a volatilising process explained in Hamer's *Dictionary*. Presumable ZnO incorporated into a frit would be largely immune from reduction. Zinc oxide (un-fritted) may be used in oxidised stoneware glazes for the following reasons:

1. Glazes high in zinc and low in alumina and silica will often develop spectacular crystals within the glass. This is the most common type of 'Crystalline Glaze'.

2. Opaque glazes with a high shine can be produced without the addition of any normal 'opacifier'.

3. Small amounts of zinc introduced into a stoneware glaze are useful in starting fusion and forming a more perfect surface.
4. Zinc has some unique effects on colouring oxides — see later.
5. Zinc can lower the coefficient of expansion of a glaze and increase the elasticity, thereby reducing or eliminating crazing. It is second only to calcium in the fluxes in promoting strength in a glaze. Thus, it is a useful flux in the development of strong uncrazed functional glazes.

Data is given for 3 sets, but only the Zinc Set is studied in full here:

Zinc Set:	**Intermediate Sets:**	
0.2 K_2O	O.2 K_2O	0.2 K_2O
0.3 CaO	0.5 CaO	0.7 CaO
0.5 ZnO	0.3 ZnO	0.1 ZnO

SOURCES OF ZINC

Zinc oxide is the main form of zinc used in ceramics although sometimes it will be introduced as part of a frit.

There are several grades of zinc oxide, depending on purity and particle size. Cheaper grades of zinc oxide may be contaminated with the oxides of iron, cadmium and lead. Inferior grades may contain considerable lead sulfate.

Potters' suppliers in Australia usually provide zinc oxide in two grades: 'colloidal' and 'dense'. The colloidal form, if used in excess, will cause severe crawling. The 'dense' grade has been calcined to overcome this problem, but may contain small lumps that need grinding; this will be detected when sieving the glaze prior to use.

DATA SHEET ZINC SET

RECIPE (%)

GLAZE No.	K FEL	WHITING	ZnO	KAOLIN	SILICA
1	33.04	8.91	12.08	45.97	.00
2	29.60	7.98	10.82	41.19	10.41
3	26.16	7.06	9.57	36.40	20.82
4	22.72	6.13	8.31	31.62	31.23
5	19.28	5.20	7.05	26.83	41.64
6	37.72	10.18	13.79	38.31	.00
7	33.41	9.01	12.22	34.32	11.05
8	29.09	7.85	10.64	30.33	22.09
9	24.77	6.68	9.06	26.35	33.14
10	20.46	5.52	7.48	22.36	44.19
11	42.41	11.44	15.51	30.65	.00
12	37.21	10.04	13.61	27.46	11.68
13	32.02	8.64	11.71	24.27	23.37
14	26.83	7.24	9.81	21.08	35.05
15	21.64	5.84	7.91	17.89	46.73
16	47.09	12.71	17.22	22.99	.00
17	41.02	11.07	15.00	20.59	12.32
18	34.95	9.43	12.78	18.20	24.64
19	28.88	7.79	10.56	15.81	36.96
20	22.82	6.16	8.34	13.42	49.28
21	51.77	13.97	18.93	15.32	.00
22	44.83	12.10	16.39	13.73	12.96
23	37.88	10.22	13.85	12.13	25.91
24	30.94	8.35	11.31	10.54	38.87
25	23.99	6.47	8.77	8.94	51.82
26	56.46	15.24	20.65	7.66	.00
27	48.64	13.12	17.79	6.86	13.59
28	40.81	11.01	14.92	6.07	27.18
29	32.99	8.90	12.06	5.27	40.77
30	25.17	6.79	9.20	4.47	54.37
31	61.14	16.50	22.36	.00	.00
32	52.44	14.15	19.18	.00	14.23
33	43.75	11.81	16.00	.00	28.46
34	35.05	9.46	12.81	.00	42.68
35	26.35	7.11	9.63	.00	56.91

OXIDE WEIGHTS (%)

GLAZE No.	K_2O	CaO	ZnO	Al_2O_3	SiO_2
1	6.24	5.57	13.47	26.98	47.74
2	5.55	4.95	11.98	23.99	53.53
3	4.86	4.34	10.49	21.01	59.32
4	4.17	3.72	8.99	18.02	65.10
5	3.48	3.10	7.50	15.03	70.89
6	7.06	6.30	15.24	24.50	46.90
7	6.21	5.54	13.41	21.71	53.13
8	5.37	4.79	11.57	18.93	59.35
9	4.52	4.03	9.74	16.14	65.58
10	3.67	3.27	7.91	13.36	71.80
11	7.88	7.04	17.01	22.01	46.06
12	6.88	6.14	14.84	19.43	52.72
13	5.87	5.24	12.66	16.85	59.39
14	4.86	4.34	10.49	14.26	66.05
15	3.86	3.44	8.31	11.68	72.71
16	8.71	7.77	18.79	19.53	45.22
17	7.54	6.73	16.27	17.15	52.32
18	6.38	5.69	13.75	14.77	59.42
19	5.21	4.65	11.24	12.39	66.52
20	4.05	3.61	8.72	10.01	73.63
21	9.53	8.50	20.56	17.04	44.38
22	8.20	7.32	17.70	14.86	51.92
23	6.88	6.14	14.84	12.69	59.46
24	5.56	4.96	11.98	10.51	67.00
25	4.23	3.77	9.13	8.33	74.54
26	10.35	9.24	22.33	14.56	43.54
27	8.87	7.91	19.13	12.58	51.52
28	7.39	6.59	15.93	10.61	59.49
29	5.90	5.27	12.73	8.63	67.47
30	4.42	3.94	9.53	6.66	75.45
31	11.17	9.97	24.10	12.07	42.70
32	9.53	8.51	20.56	10.30	51.12
33	7.89	7.04	17.02	8.53	59.53
34	6.25	5.58	13.48	6.75	67.95
35	4.61	4.11	9.94	4.98	76.36

Alumina/Silica (M.P.) Figures same as for 0.8 Limestone Set.

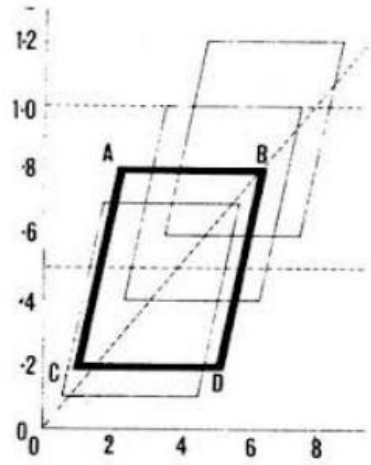
EXPERIMENT NO. 7 THE ZINC SET

Corner Glazes — The limits of the experiment:

	RECIPE (%)					OXIDE WT. (%)					M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	ZINC OXIDE	KAOLIN	SILICA	K_2O	CaO	ZnO	Al_2O_3	SiO_2	FLUXES: 0.2 K_2O 0.3 CaO 0.5 ZnO
											Al_2O_3/SiO_2:
A	33.04	8.91	12.08	45.97	0	6.24	5.57	13.47	26.98	47.74	0.8/2.4
B	19.28	5.20	7.05	26.83	41.64	3.48	3.10	7.50	15.03	70.89	0.8/6.4
C	61.14	16.50	22.36	0	0	11.17	9.97	24.10	12.07	42.70	0.2/1.2
D	26.35	7.11	9.63	0	56.91	4.61	4.11	9.94	4.98	76.36	0.2/5.2

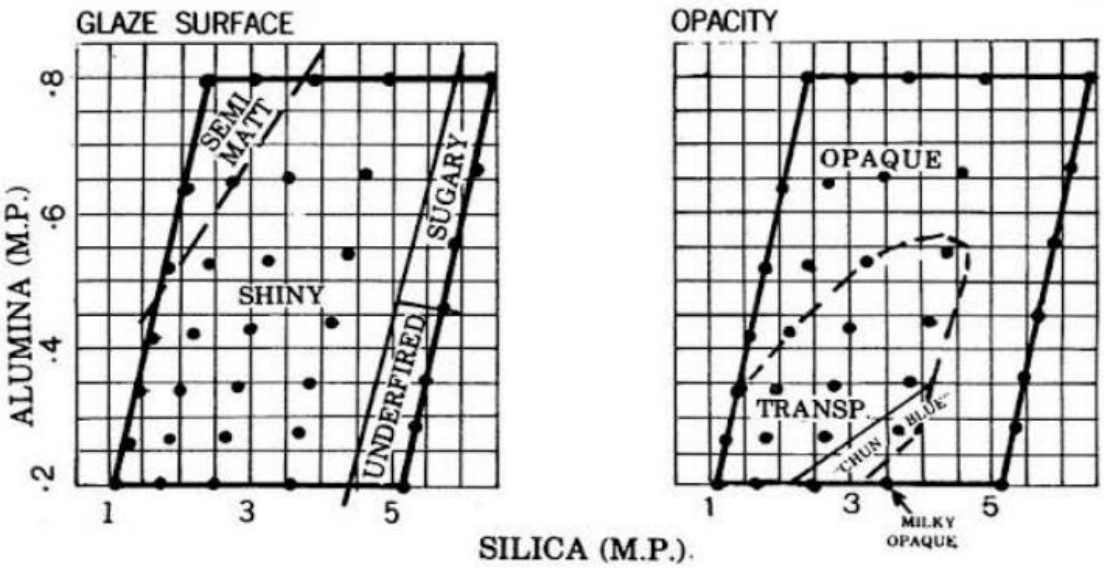
See 'Preliminary Comments on Experiments' (Chapter 8) for experimental details including explanation of data and charts presented here.

Grid Location Diagram:



Results Charts:

Firing 4: 1280°C (2336°F)



ZINC SET

Comments on Results

See diagrams opposite.

1. As Hamer points out in his *Potter's Dictionary*, zinc oxide fired in reduction is rapidly reduced to the metal, which volatilises from the glaze at temperatures over 950°C. (1742°F). Presumably there may be some marginal effects where some zinc oxide may be retained with late or light reduction; however, this set of glazes fired in heavy reduction in Firing 1 looks as though the zinc has completely disappeared, giving an extended version of the 0.6 Limestone Set:

0.2 K_2O 0.3 CaO 0.5 ZnO	minus 0.5 ZnO	=	0.2 K_2O 0.3 CaO
multiplied by 2 (to regain unity)		=	0.4 K_2O 0.6 CaO
		=	the 0.6 Limestone Set of fluxes

The only results given here are for Firing 4, an oxidising firing otherwise equivalent to (reduction) Firing 1.

2. The role of zinc as an opacifier is very evident, especially in the high alumina corner.

3. The efficiency of zinc as a flux may be seen by comparison with the other sets using the same baseline grid (Barium, Magnesium and 0.8 Limestone Sets). In particular, zinc oxide seems very efficient at fluxing high alumina glazes, which have here a shine and opacity not equalled in the other sets.

4. The opacifying nature of zinc oxide is also responsible for the easy development of Chun-blue in these glazes. In oxidised Firing 4, Chun-blue effect is developed in Glazes 29 and 33. Addition of rutile or titanium dioxide (even by brush) will often cause Chun-blue to develop in the transparent glazes.

5. There are no truly matt glazes in the set at this temperature (Firing 4). Lower temperatures should produce some alumina matts, and some large crystal growth in the low alumina, low silica glazes. See Chapter 16 for more on Zinc Crystal Glazes.

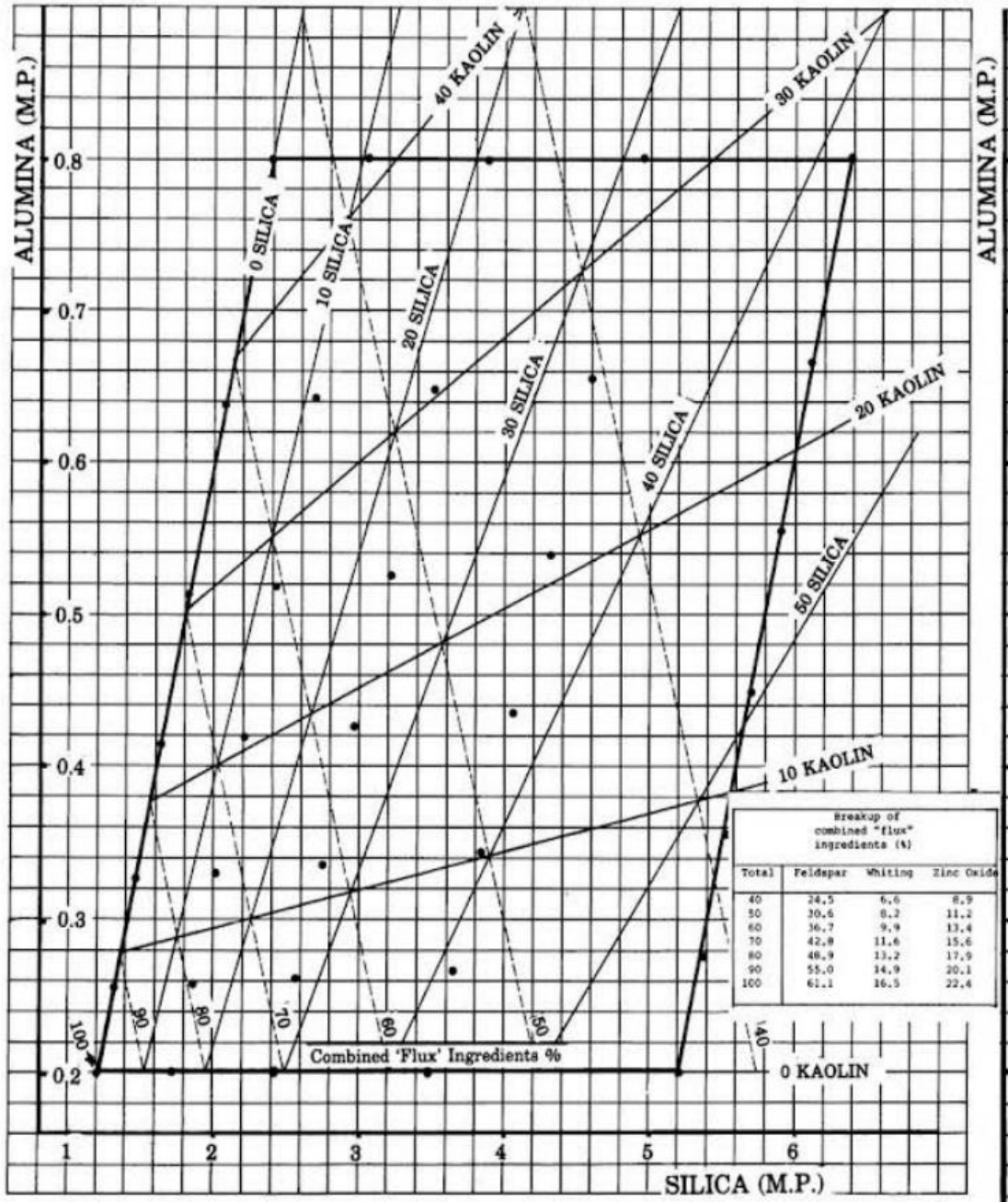
6. The effect of zinc on colouring oxides in glazes is fairly unique, sometimes beneficial, sometimes unpleasant. Colours will tend to be less brilliant, more pastel. You should get a lighter shade of blue from cobalt. Chrome will tend to give tans and browns. Cobalt and chrome together seemed to give an interesting reaction. Some interesting effects were noted with nickel oxide — some greens, and perhaps some purples in the Chun-blue glazes.

7. Colloidal zinc oxide causes severe crawling in the high clay glazes, crawling that does not heal over with increased temperature. If this proves a problem, use of 'dense' grade will overcome it, bearing in mind of course that high clay content itself is a cause of crawling unless the clay content is wholly or partly calcined.

8. Of the eight sets studied here, the zinc set exhibits least crazing (see Diagram 7.2). Zinc can therefore play a useful role in adjusting glaze fit.

ZINC SET

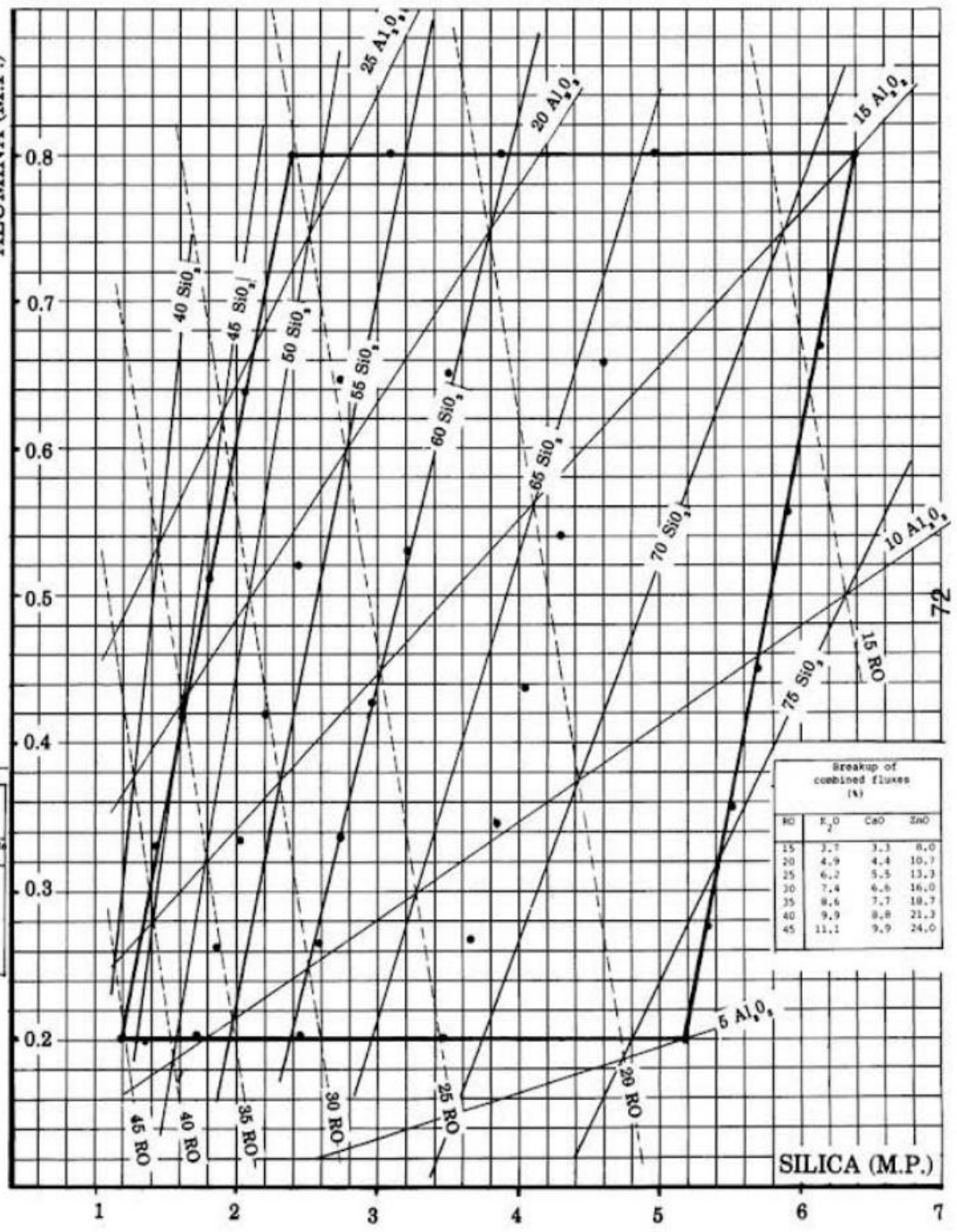
RECIPE CHART



Breakup of combined "flux" ingredients (%)

Total	Feldspar	Whiting	Zinc Oxide
40	24.5	6.6	8.9
50	30.6	8.2	11.2
60	36.7	9.9	13.4
70	42.8	11.6	15.6
80	48.9	13.2	17.9
90	55.0	14.9	20.1
100	61.1	16.5	22.4

OXIDE WEIGHTS CHART



Breakup of combined fluxes (%)

RO	K_2O	CaO	ZnO
15	3.7	3.3	8.0
20	4.9	4.4	10.7
25	6.2	5.5	13.3
30	7.4	6.6	16.0
35	8.6	7.7	18.7
40	9.9	8.8	21.3
45	11.1	9.9	24.0

ZINC GLAZES -- INTERMEDIATE SETS

0.3 Zinc Set (0.2 K_2O, 0.5 CaO, 0.3 ZnO)

	RECIPES (%)					OXIDE WTS (%)				
	K FEL	WHITING	ZnO	KAOLIN	SILICA	K_2O	CaO	ZnO	Al_2O_3	SiO_2
1	32.67	14.69	7.17	45.46	.00	6.35	9.44	8.22	27.44	48.55
2	29.29	13.17	6.43	40.76	10.34	5.64	8.39	7.30	24.37	54.30
3	25.92	11.65	5.69	36.06	20.69	4.93	7.33	6.38	21.31	60.06
4	22.54	10.13	4.94	31.35	31.03	4.22	6.28	5.46	18.24	65.81
5	19.16	8.61	4.20	26.65	41.37	3.51	5.22	4.54	15.17	71.56
6	37.21	16.73	8.17	37.88	.00	7.21	10.72	9.34	24.94	47.80
7	32.99	14.83	7.24	33.96	10.97	6.33	9.42	8.20	22.08	53.98
8	28.77	12.93	6.31	30.05	21.94	5.46	8.11	7.06	19.21	60.16
9	24.54	11.03	5.38	26.13	32.91	4.58	6.81	5.93	16.35	66.34
10	20.32	9.13	4.46	22.21	43.88	3.70	5.51	4.79	13.48	72.52
11	41.75	18.77	9.16	30.31	.00	8.07	12.00	10.45	22.44	47.04
12	36.68	16.49	8.05	27.17	11.60	7.03	10.45	9.10	19.78	53.65
13	31.62	14.21	6.94	24.04	23.19	5.98	8.90	7.75	17.12	60.26
14	26.55	11.93	5.82	20.90	34.79	4.94	7.35	6.39	14.46	66.87
15	21.48	9.65	4.71	17.77	46.38	3.90	5.79	5.04	11.79	73.48
16	46.29	20.82	10.16	22.73	.00	8.93	13.28	11.57	19.94	46.29
17	40.38	18.16	8.86	20.38	12.22	7.72	11.48	10.00	17.48	53.32
18	34.47	15.50	7.56	18.03	24.45	6.51	9.68	8.43	15.02	60.36
19	28.55	12.84	6.26	15.68	36.67	5.30	7.88	6.86	12.56	67.40
20	22.64	10.18	4.97	13.33	48.89	4.09	6.08	5.29	10.11	74.44
21	50.83	22.86	11.16	15.15	.00	9.79	14.56	12.68	17.44	45.53
22	44.07	19.82	9.67	13.59	12.85	8.41	12.51	10.90	15.18	53.00
23	37.32	16.78	8.19	12.02	25.70	7.04	10.46	9.11	12.93	60.46
24	30.56	13.74	6.70	10.45	38.55	5.66	8.42	7.33	10.67	67.93
25	23.80	10.70	5.22	8.88	51.40	4.28	6.37	5.54	8.42	75.39
26	55.37	24.90	12.15	7.58	.00	10.65	15.84	13.80	14.94	44.78
27	47.77	21.48	10.48	6.79	13.48	9.11	13.54	11.79	12.89	52.67
28	40.17	18.06	8.81	6.01	26.95	7.56	11.25	9.79	10.83	60.56
29	32.56	14.64	7.14	5.23	40.43	6.02	8.95	7.79	8.78	68.46
30	24.96	11.22	5.48	4.44	53.90	4.48	6.65	5.79	6.73	76.35
31	59.91	26.94	13.15	.00	.00	11.51	17.12	14.91	12.44	44.02
32	51.46	23.14	11.30	.00	14.10	9.80	14.58	12.69	10.59	52.34
33	43.02	19.34	9.44	.00	28.21	8.09	12.03	10.48	8.74	60.67
34	34.57	15.54	7.59	.00	42.31	6.38	9.49	8.26	6.89	68.99
35	26.12	11.74	5.73	.00	56.41	4.67	6.94	6.04	5.04	77.31

0.1 Zinc Set (0.2 K_2O, 0.7 CaO, 0.1 ZnO)

	RECIPES (%)					OXIDE WTS (%)				
	K FEL	WHITING	ZnO	KAOLIN	SILICA	K_2O	CaO	ZnO	Al_2O_3	SiO_2
1	32.32	20.35	2.36	44.97	.00	6.46	13.45	2.79	27.91	49.39
2	29.00	18.26	2.12	40.35	10.28	5.73	11.93	2.48	24.76	55.10
3	25.68	16.17	1.88	35.73	20.56	5.00	10.42	2.16	21.61	60.82
4	22.35	14.07	1.63	31.10	30.83	4.27	8.90	1.85	18.46	66.53
5	19.03	11.98	1.39	26.48	41.11	3.54	7.38	1.53	15.31	72.24
6	36.72	23.12	2.68	37.48	.00	7.36	15.33	3.18	25.40	48.73
7	32.58	20.52	2.38	33.62	10.89	6.46	13.45	2.79	22.45	54.86
8	28.45	17.91	2.08	29.77	21.79	5.55	11.56	2.40	19.50	60.99
9	24.31	15.31	1.78	25.92	32.68	4.64	9.68	2.01	16.56	67.12
10	20.17	12.70	1.47	22.07	43.58	3.74	7.79	1.62	13.61	73.25
11	41.12	25.89	3.01	29.98	.00	8.27	17.21	3.57	22.89	48.07
12	36.17	22.77	2.64	26.90	11.51	7.18	14.96	3.10	20.14	54.61
13	31.22	19.66	2.28	23.82	23.02	6.10	12.71	2.64	17.40	61.16
14	26.27	16.54	1.92	20.74	34.54	5.02	10.45	2.17	14.65	67.71
15	21.32	13.42	1.56	17.65	46.05	3.93	8.20	1.70	11.91	74.26
16	45.53	28.66	3.33	22.49	.00	9.17	19.09	3.96	20.38	47.41
17	39.76	25.03	2.91	20.17	12.13	7.91	16.47	3.42	17.83	54.37
18	33.99	21.40	2.49	17.86	24.26	6.65	13.85	2.87	15.29	61.34
19	28.23	17.77	2.06	15.55	36.39	5.39	11.23	2.33	12.75	68.30
20	22.46	14.14	1.64	13.24	48.52	4.13	8.61	1.79	10.21	75.27
21	49.93	31.43	3.65	14.99	.00	10.07	20.97	4.35	17.86	46.74
22	43.35	27.29	3.17	13.45	12.75	8.64	17.98	3.73	15.53	54.13
23	36.77	23.15	2.69	11.91	25.49	7.20	15.00	3.11	13.19	61.51
24	30.18	19.00	2.21	10.37	38.24	5.76	12.01	2.49	10.85	68.89
25	23.60	14.86	1.72	8.83	50.98	4.33	9.02	1.87	8.51	76.27
26	54.33	34.20	3.98	7.50	.00	10.98	22.85	4.74	15.35	46.08
27	46.93	29.55	3.43	6.72	13.36	9.36	19.50	4.04	13.22	53.88
28	39.54	24.89	2.89	5.95	26.73	7.75	16.14	3.35	11.08	61.68
29	32.14	20.24	2.35	5.18	40.09	6.14	12.79	2.65	8.95	69.48
30	24.75	15.58	1.81	4.41	53.45	4.52	9.43	1.96	6.81	77.28
31	58.73	36.97	4.30	.00	.00	11.88	24.73	5.13	12.84	45.42
32	50.52	31.80	3.70	.00	13.98	10.09	21.01	4.36	10.91	53.64
33	42.31	26.64	3.10	.00	27.96	8.30	17.29	3.59	8.98	61.86
34	34.10	21.47	2.49	.00	41.94	6.51	13.56	2.81	7.04	70.07
35	25.89	16.30	1.89	.00	55.92	4.72	9.84	2.04	5.11	78.29

Alumina/Silica (M.P.) Figures same as for 0.8 Limestone Set

11 BARIUM GLAZES

In many ways, barium oxide is similar in effect to calcium oxide in stoneware glazes; however, under favourable conditions (such as high temperature or being used in a frit) it is a somewhat more vigorous flux and can give brighter, shinier glazes than calcium. Some barium glazes give slightly unusual effects with some colouring oxides rather similar to the alkaline (R_2O) fluxes. Some excellent matt glazes are possible with BaO. Barium oxide is very effective (like CaO) in dissolving iron oxide, rather than letting it crystallise out.

Data is given for 3 sets, but only the Barium Set is studied in full here:

Barium Set:	**Intermediate Sets:**	
0.2 K_2O	0.2 K_2O	0.2 K_2O
0.3 CaO	0.5 CaO	0.7 CaO
0.5 BaO	0.3 BaO	0.1 BaO

SOURCES OF BARIUM

Barium carbonate is the most common source of barium oxide for most glazes. The carbonate does occur in nature as the mineral witherite ($BaCO_3$) and this is prepared for industrial use. However, most commercial $BaCO_3$ is prepared by chemical reaction from the mineral barite, or barytes (barium sulphate, $BaSO_4$), which is a common and widely distributed mineral. Barium carbonate prepared from this source usually contains some sulphur.

Barium oxide is also available incorporated into frits, but these are not generally available here except with the barium as a relatively minor flux.

There is a barium feldspar, celsian ($BaO.Al_2O_3.2SiO_2$), but this is rare and not a practical source of BaO.

BARIUM CARBONATE IS POISONOUS

The following extract is from *Pottery in Australia,* Vol. 17/2, from an article by W.C. Alexander, 'Ceramic Toxicology'.

> 'Barium carbonate is the usual source of Ba in ceramic usage. It, along with barium chloride and barium hydroxide, is partially soluble and may be a deadly poison. If completely absorbed into the system, as little as one gram can be fatal. The first symptoms are tremors followed by convulsions and, in terminal cases, death due to cardiac and/or respiratory failures.
>
> Inhaled barium compounds are also dangerous but are not usually absorbed into the system, and hence, not fatal. They produce "baritosis", a benign form of pneumoconiosis associated with barite.'

Just how much barium carbonate you would have to swallow to 'completely absorb' one gram I do not know, but I recommend care in its use; use rubber gloves with barium carbonate or barium glazes; do not eat or drink or smoke while using them, and keep dust down.

Barium carbonate by itself has a decomposition temperature of 1421°C, and when used raw in a glaze (i.e. not incorporated into a frit), some of it may persist during and even after the maturing of the glaze. Bearing in mind the poisonous nature of $BaCO_3$, this makes for a possibly dangerous situation, especially with some 'modern' barium matt glazes that have very high percentages of this material. It is virtually certain that such glazes contain unfused $BaCO_3$ that could be leached out into certain foods and drinks if used in functional ware. Until more is known about this, my recommendation is that barium matt glazes not be used inside functional ware.

BARIUM GLAZES – INTERMEDIATE SETS

0.3 Barium Set (0.2 K_2O, 0.5 CaO, 0.3 BaO)

RECIPES (%)

	K FEL	WHITING	BaCO3	KAOLIN	SILICA
1	29.65	13.33	15.77	41.25	.00
2	26.76	12.03	14.23	37.23	9.76
3	23.86	10.73	12.70	33.20	19.52
4	20.97	9.43	11.16	29.18	29.28
5	18.07	8.13	9.62	25.15	39.04
6	33.12	14.89	17.62	34.38	.00
7	29.61	13.31	15.75	31.02	10.31
8	26.10	11.74	13.89	27.67	20.61
9	22.59	10.16	12.02	24.31	30.92
10	19.08	8.59	10.16	20.96	41.23
11	36.59	16.45	19.46	27.50	.00
12	32.46	14.60	17.27	24.82	10.85
13	28.34	12.75	15.08	22.13	21.71
14	24.22	10.89	12.89	19.45	32.56
15	20.09	9.04	10.70	16.77	43.41
16	40.06	18.01	21.31	20.63	.00
17	35.32	15.88	18.79	18.61	11.40
18	30.58	13.75	16.27	16.60	22.80
19	25.84	11.62	13.75	14.59	34.20
20	21.11	9.50	11.24	12.58	45.60
21	43.52	19.57	23.16	13.75	.00
22	38.17	17.17	20.31	12.41	11.95
23	32.82	14.76	17.47	11.07	23.89
24	27.47	12.36	14.62	9.73	35.84
25	22.12	9.95	11.77	8.38	47.78
26	46.99	21.13	25.00	6.88	.00
27	41.03	18.45	21.83	6.20	12.49
28	35.06	15.77	18.66	5.53	24.98
29	29.09	13.09	15.48	4.86	37.47
30	23.13	10.41	12.31	4.19	49.97
31	50.46	22.69	26.85	.00	.00
32	43.88	19.73	23.35	.00	13.04
33	37.30	16.78	19.85	.00	26.08
34	30.72	13.82	16.35	.00	39.11
35	24.14	10.86	12.85	.00	52.15

OXIDE WTS (%)

	K_2O	CaO	BaO	Al_2O_3	SiO_2
1	5.92	8.80	14.44	25.58	45.26
2	5.28	7.86	12.89	22.83	51.15
3	4.65	6.91	11.34	20.08	57.03
4	4.01	5.97	9.78	17.33	62.92
5	3.37	5.02	8.23	14.58	68.80
6	6.63	9.86	16.17	23.15	44.20
7	5.86	8.71	14.29	20.60	50.54
8	5.09	7.57	12.42	18.05	56.88
9	4.32	6.43	10.54	15.50	63.22
10	3.55	5.28	8.66	12.95	69.57
11	7.34	10.91	17.90	20.72	43.14
12	6.43	9.57	15.70	18.37	49.94
13	5.53	8.23	13.50	16.02	56.73
14	4.63	6.89	11.29	13.67	63.53
15	3.72	5.54	9.09	11.32	70.33
16	8.05	11.97	19.63	18.29	42.08
17	7.01	10.43	17.10	16.14	49.33
18	5.97	8.89	14.58	13.99	56.59
19	4.94	7.35	12.05	11.84	63.84
20	3.90	5.81	9.52	9.69	71.10
21	8.75	13.02	21.36	15.85	41.01
22	7.58	11.28	18.51	13.90	48.73
23	6.42	9.54	15.66	11.95	56.44
24	5.25	7.81	12.80	10.00	64.15
25	4.08	6.07	9.95	8.05	71.86
26	9.46	14.08	23.09	13.42	39.95
27	8.16	12.14	19.91	11.67	48.12
28	6.86	10.20	16.74	9.92	56.29
29	5.56	8.27	13.56	8.17	64.46
30	4.25	6.33	10.38	6.42	72.63
31	10.17	15.13	24.82	10.99	38.89
32	8.74	13.00	21.32	9.44	47.52
33	7.30	10.86	17.82	7.89	56.14
34	5.87	8.73	14.31	6.34	64.77
35	4.43	6.59	10.81	4.79	73.39

0.1 Barium Set (0.2 K_2O, 0.7 CaO, 0.1 BaO)

RECIPES (%)

	K FEL	WHITING	BaCO3	KAOLIN	SILICA
1	31.27	19.68	5.55	43.50	.00
2	28.12	17.70	4.99	39.12	10.08
3	24.97	15.72	4.43	34.74	20.16
4	21.81	13.73	3.87	30.35	30.23
5	18.66	11.75	3.31	25.97	40.31
6	35.28	22.21	6.26	36.25	.00
7	31.40	19.76	5.57	32.60	10.67
8	27.52	17.32	4.88	28.95	21.33
9	23.63	14.88	4.19	25.29	32.00
10	19.75	12.44	3.50	21.64	42.67
11	39.29	24.73	6.97	29.00	.00
12	34.68	21.83	6.15	26.08	11.26
13	30.07	18.93	5.34	23.16	22.51
14	25.46	16.03	4.52	20.24	33.77
15	20.84	13.12	3.70	17.31	45.02
16	43.31	27.26	7.69	21.75	.00
17	37.96	23.90	6.74	19.56	11.85
18	32.62	20.54	5.79	17.37	23.69
19	27.28	17.17	4.84	15.18	35.54
20	21.94	13.81	3.89	12.99	47.38
21	47.32	29.79	8.40	14.50	.00
22	41.24	25.96	7.32	13.04	12.43
23	35.17	22.14	6.24	11.58	24.87
24	29.10	18.32	5.16	10.12	37.30
25	23.03	14.50	4.08	8.66	49.74
26	51.33	32.31	9.11	7.25	.00
27	44.53	28.03	7.90	6.52	13.02
28	37.72	23.75	6.69	5.79	26.05
29	30.92	19.47	5.48	5.06	39.07
30	24.12	15.18	4.28	4.33	52.09
31	55.34	34.84	9.82	.00	.00
32	47.81	30.10	8.48	.00	13.61
33	40.28	25.36	7.15	.00	27.23
34	32.74	20.61	5.81	.00	40.84
35	25.21	15.87	4.47	.00	54.45

OXIDE WTS (%)

	K_2O	CaO	BaO	Al_2O_3	SiO_2
1	6.30	13.12	5.13	27.24	48.20
2	5.60	11.66	4.56	24.21	53.97
3	4.90	10.20	3.99	21.18	59.74
4	4.19	8.74	3.41	18.14	65.51
5	3.49	7.28	2.84	15.11	71.28
6	7.14	14.88	5.82	24.75	47.41
7	6.28	13.08	5.11	21.92	53.61
8	5.41	11.28	4.41	19.09	59.81
9	4.55	9.48	3.70	16.26	66.02
10	3.68	7.68	3.00	13.43	72.22
11	7.99	16.63	6.50	22.25	46.62
12	6.96	14.49	5.66	19.63	53.25
13	5.93	12.35	4.83	17.00	59.89
14	4.90	10.21	3.99	14.37	66.52
15	3.87	8.07	3.15	11.75	73.16
16	8.83	18.39	7.19	19.76	45.83
17	7.64	15.91	6.22	17.34	52.89
18	6.45	13.43	5.25	14.91	59.96
19	5.26	10.95	4.28	12.49	67.03
20	4.07	8.47	3.31	10.07	74.10
21	9.67	20.15	7.87	17.27	45.03
22	8.32	17.33	6.77	15.05	52.53
23	6.97	14.51	5.67	12.83	60.03
24	5.61	11.69	4.56	10.60	67.53
25	4.26	8.87	3.46	8.38	75.03
26	10.52	21.90	8.56	14.77	44.24
27	9.00	18.74	7.32	12.76	52.17
28	7.48	15.58	6.09	10.74	60.11
29	5.97	12.42	4.85	8.72	68.04
30	4.45	9.26	3.62	6.70	75.97
31	11.36	23.66	9.24	12.28	43.45
32	9.68	20.16	7.87	10.47	51.82
33	8.00	16.66	6.51	8.65	60.18
34	6.32	13.16	5.14	6.84	68.55
35	4.64	9.66	3.77	5.02	76.91

Alumina/Silica (M.P.) Figures same as for 0.8 Limestone Set.

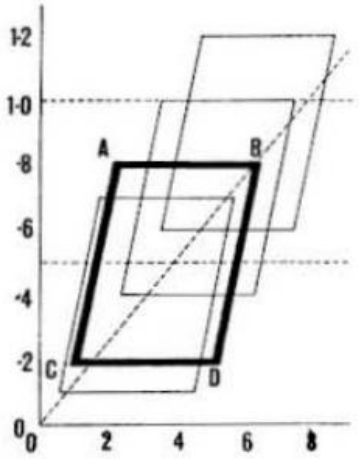
EXPERIMENT NO. 8 THE BARIUM SET

Corner Glazes — The limits of the experiment:

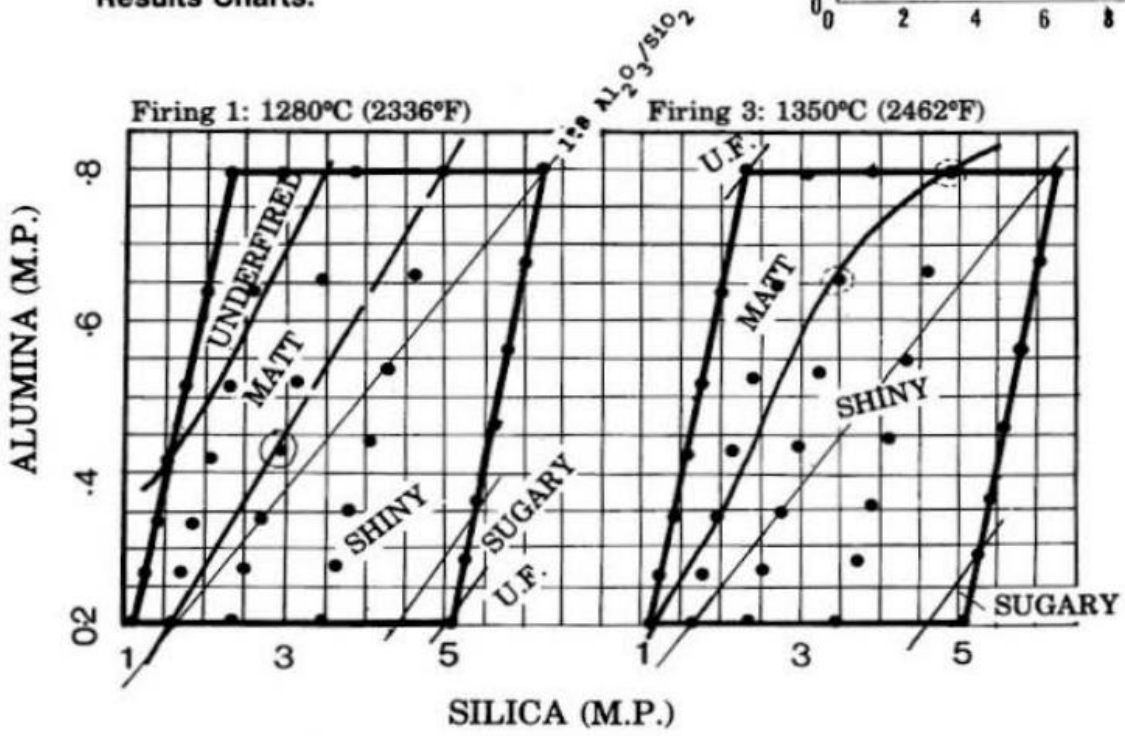
	RECIPE (%)					OXIDE WT. (%)					M.P.
CORNER GLAZES	POTASH FELDSPAR	WHITING	BARIUM CARB.	KAOLIN	SILICA	K_2O	CaO	BaO	Al_2O_3	SiO_2	FLUXES: 0.2 K_2O 0.3 CaO 0.5 BaO
											Al_2O_3/SiO_2:
A	28.19	7.60	24.99	39.22	0	5.58	4.98	22.68	24.11	42.66	0.8/2.4
B	17.52	4.73	15.54	24.38	37.84	3.26	2.91	13.26	14.09	66.48	0.8/6.4
C	46.37	12.51	41.12	0	0	9.20	8.21	37.43	9.95	35.20	0.2/1.2
D	23.17	6.25	20.54	0	50.04	4.24	3.78	17.22	4.58	70.18	0.2/5.2

See 'Preliminary Comments on Experiments' (Chapter 8) for experimental details including explanation of data and charts presented here.

Grid Location Diagram:



Results Charts:



BARIUM SET

Comments on Results

See diagrams opposite.

1. The barium set produces some excellent alumina matt glazes, but unlike the magnesium set, or the 0.8 Limestone Set, produces no silica matts, there being a sharp transition from shiny glazes to sugary or underfired glazes as silica increases.
2. The barium alumina and flux matts seem to keep their mattness over a wider range of temperatures, especially if compared with the magnesium glazes, and to a lesser extent the 0.8 Limestone Set.
3. BaO is similar to CaO in that it helps iron dissolve rather than crystallise. This is evident in lower alumina glazes, where iron greens and blues may result in reduction.
4. Low alumina barium glazes give some typically alkaline colour responses, even though it belongs to the RO, rather than to the R_2O group of fluxes. In oxidation, purple is possible with manganese, yellows with a little iron, aqua and turquoise with copper, and also a soft yellow-green with a little chrome. In many glazes, chrome remains unfused, giving a dense opaque green. If used sparingly, soft yellow-green is obtained in low alumina barium glazes. The colour relies on the chrome being dissolved into the glaze. The effect is fairly delicate and needs a white body, or slip, underneath.
5. Cobalt typically gives brighter blues in barium glazes than it does in the other sets.
6. Considerable vaporisation of the BaO is evident as an apricot blush on the porcelain clay around the edges of the glaze, especially around Corner C,which is high in fluxes.
7. A good 'orange-peel' effect is obtained on Glaze 18 in Firing 1.
8. Matt pink glazes along the kaolin baseline are relatively few in the barium set. However, pink crystals up to 1 mm across occur in Glazes 21, and 26 in Firing 1, and subdued pinks occur in Glazes 6 and 11 in Firing 3.

DATA SHEET — BARIUM SET

RECIPE (%)

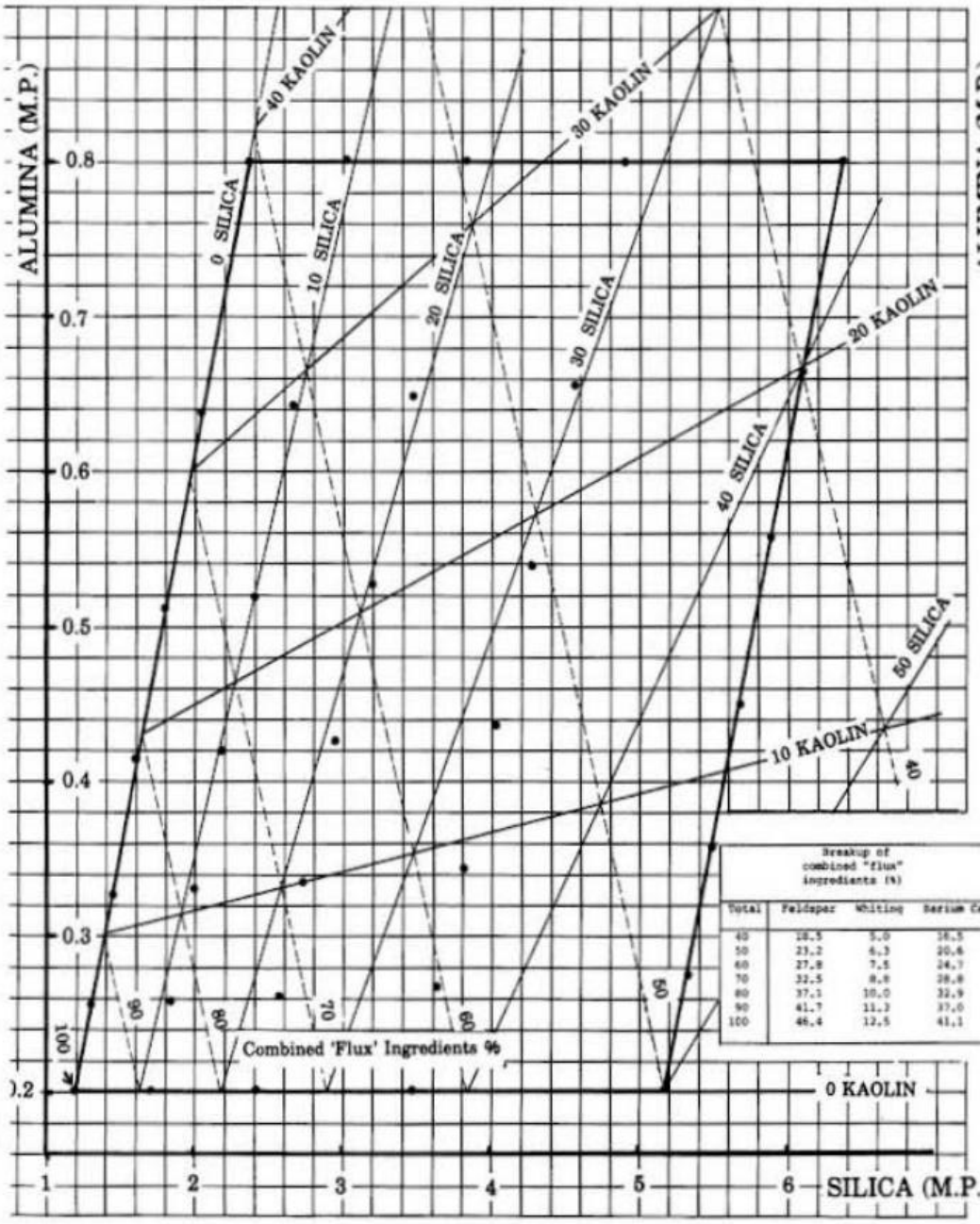
GLAZE No.	K FEL	WHITING	BaCO3	KAOLIN	SILICA
1	28.19	7.60	24.99	39.22	.00
2	25.52	6.88	22.63	35.51	9.46
3	22.86	6.17	20.27	31.80	18.92
4	20.19	5.45	17.90	28.09	28.38
5	17.52	4.73	15.54	24.38	37.84
6	31.22	8.42	27.68	32.68	.00
7	28.03	7.56	24.85	29.59	9.97
8	24.84	6.70	22.03	26.50	19.94
9	21.65	5.84	19.20	23.41	29.91
10	18.46	4.98	16.37	20.32	39.87
11	34.25	9.24	30.37	26.15	.00
12	30.54	8.24	27.08	23.67	10.48
13	26.83	7.24	23.79	21.20	20.95
14	23.12	6.24	20.50	18.73	31.43
15	19.40	5.24	17.21	16.25	41.91
16	37.28	10.06	33.06	19.61	.00
17	33.05	8.91	29.30	17.76	10.99
18	28.81	7.77	25.55	15.90	21.97
19	24.58	6.63	21.79	14.05	32.96
20	20.35	5.49	18.04	12.19	43.94
21	40.31	10.87	35.74	13.07	.00
22	35.55	9.59	31.53	11.84	11.49
23	30.80	8.31	27.31	10.60	22.99
24	26.04	7.03	23.09	9.36	34.48
25	21.29	5.74	18.87	8.13	45.97
26	43.34	11.69	38.43	6.54	.00
27	38.06	10.27	33.75	5.92	12.00
28	32.78	8.84	29.07	5.30	24.00
29	27.51	7.42	24.39	4.68	36.01
30	22.23	6.00	19.71	4.06	48.01
31	46.37	12.51	41.12	.00	.00
32	40.57	10.95	35.98	.00	12.51
33	34.77	9.38	30.83	.00	25.02
34	28.97	7.82	25.69	.00	37.53
35	23.17	6.25	20.54	.00	50.04

OXIDE WEIGHTS (%)

GLAZE No.	K_2O	CaO	BaO	Al_2O_3	SiO_2
1	5.58	4.98	22.68	24.11	42.66
2	5.00	4.46	20.33	21.61	48.62
3	4.42	3.95	17.97	19.10	54.57
4	3.84	3.43	15.62	16.60	60.53
5	3.26	2.91	13.26	14.09	66.48
6	6.18	5.52	25.14	21.75	41.42
7	5.49	4.90	22.33	19.44	47.84
8	4.80	4.29	19.53	17.13	54.26
9	4.11	3.67	16.72	14.82	60.68
10	3.42	3.06	13.92	12.51	67.10
11	6.79	6.06	27.60	19.39	40.17
12	5.99	5.34	24.34	17.27	47.06
13	5.19	4.63	21.09	15.16	53.94
14	4.39	3.91	17.83	13.04	60.83
15	3.59	3.20	14.58	10.92	67.71
16	7.39	6.60	30.06	17.03	38.93
17	6.48	5.78	26.35	15.11	46.28
18	5.57	4.97	22.65	13.18	53.63
19	4.66	4.16	18.94	11.26	60.98
20	3.75	3.35	15.24	9.34	68.33
21	7.99	7.13	32.51	14.67	37.69
22	6.97	6.22	28.36	12.94	45.50
23	5.95	5.31	24.21	11.21	53.32
24	4.93	4.40	20.05	9.48	61.13
25	3.91	3.49	15.90	7.75	68.95
26	8.60	7.67	34.97	12.31	36.44
27	7.47	6.66	30.37	10.77	44.72
28	6.34	5.65	25.77	9.24	53.00
29	5.21	4.64	21.16	7.70	61.28
30	4.08	3.64	16.56	6.17	69.56
31	9.20	8.21	37.43	9.95	35.20
32	7.96	7.10	32.38	8.61	43.95
33	6.72	6.00	27.33	7.27	52.69
34	5.48	4.89	22.27	5.92	61.44
35	4.24	3.78	17.22	4.58	70.18

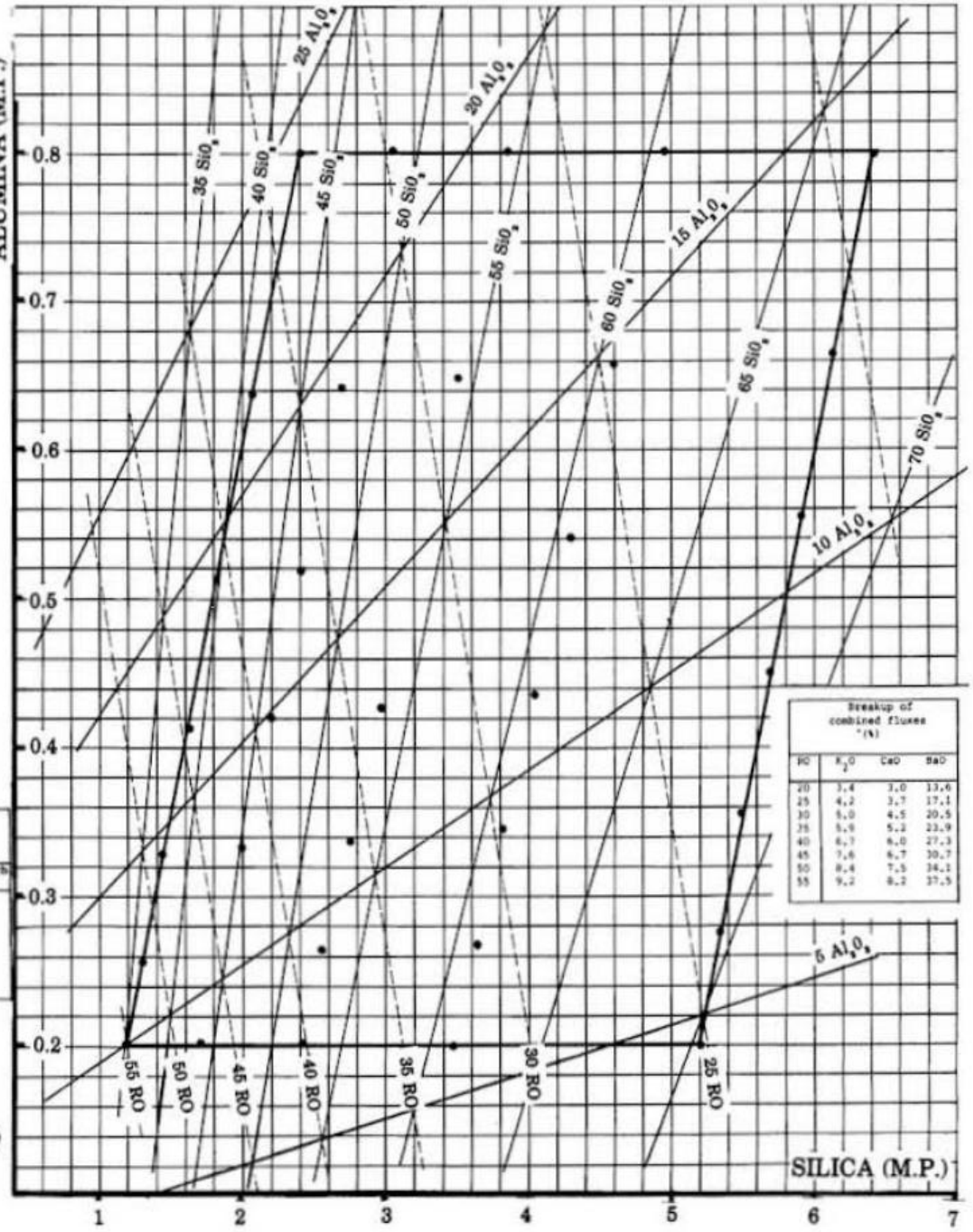
M.P.

Alumina/Silica (M.P.) Figures same as for the 0.8 Limestone Set



Breakup of combined "flux" ingredients (%)

Total	Feldspar	Whiting	Barium Carb.
40	18.5	5.0	16.5
50	23.2	6.3	20.6
60	27.8	7.5	24.7
70	32.5	8.8	28.8
80	37.1	10.0	32.9
90	41.7	11.3	37.0
100	46.4	12.5	41.1



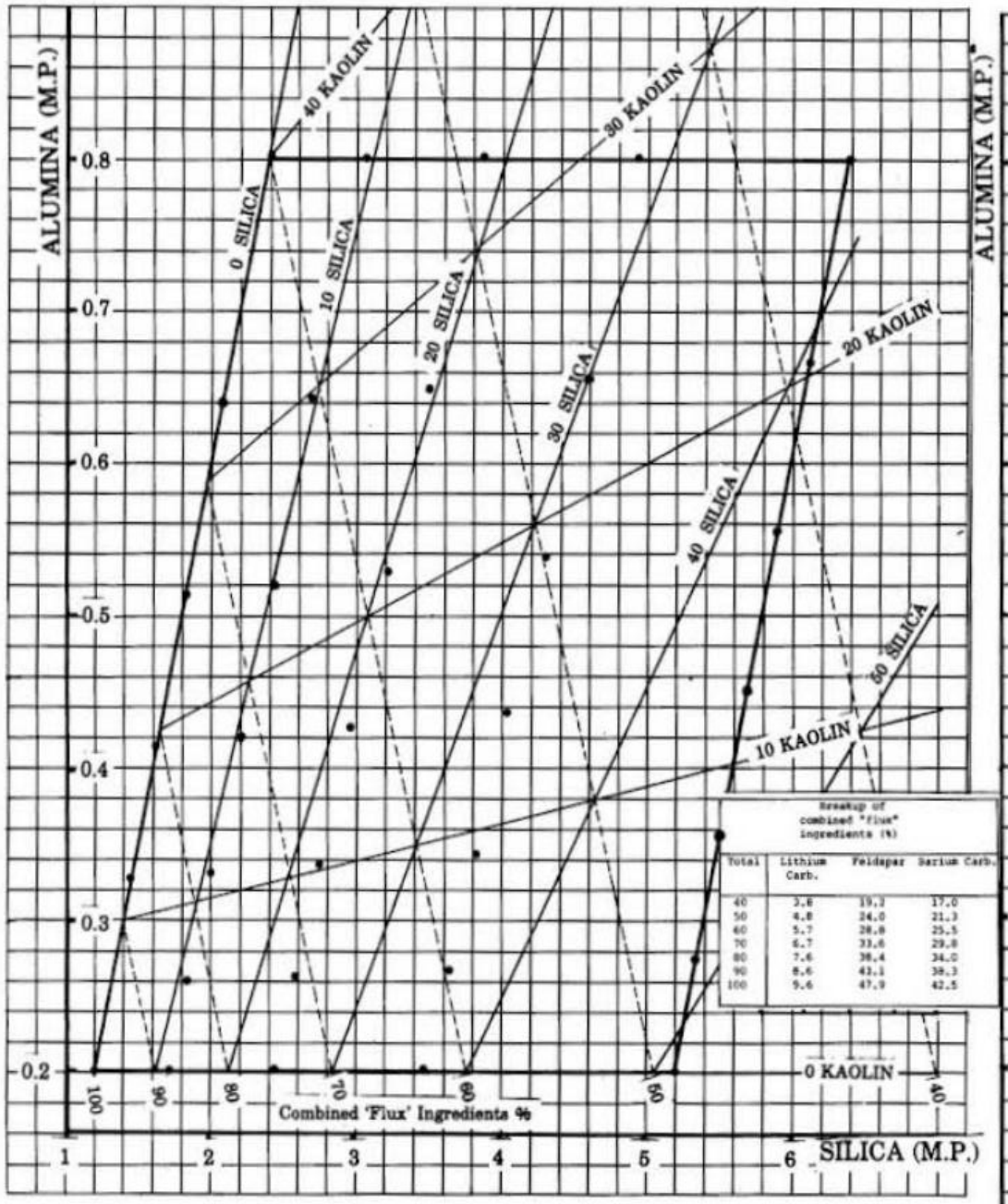
Breakup of combined fluxes (%)

RO	K_2O	CaO	BaO
20	3.4	3.0	13.6
25	4.2	3.7	17.1
30	5.0	4.5	20.5
35	5.9	5.2	23.9
40	6.7	6.0	27.3
45	7.6	6.7	30.7
50	8.4	7.5	34.1
55	9.2	8.2	37.5

RECIPE CHART

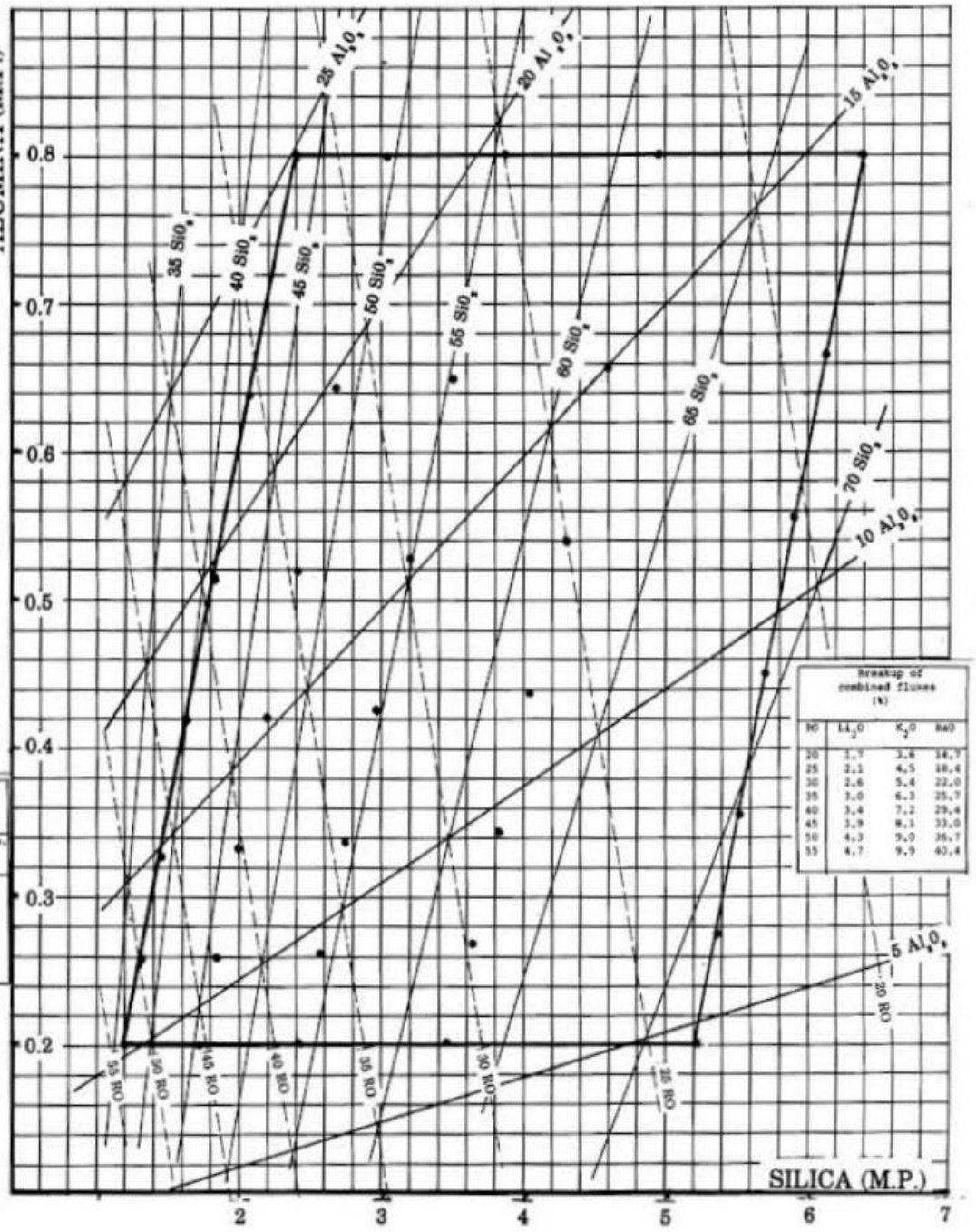
BARIUM-ALKALINE SET

OXIDE WEIGHTS CHART



Breakup of combined "flux" ingredients (%)

Total	Lithium Carb.	Feldspar	Barium Carb.
40	3.8	19.2	17.0
50	4.8	24.0	21.3
60	5.7	28.8	25.5
70	6.7	33.6	29.8
80	7.6	38.4	34.0
90	8.6	43.1	38.3
100	9.6	47.9	42.5



Breakup of combined fluxes (%)

RO	Li_2O	K_2O	BaO
20	1.9	3.6	14.9
25	2.1	4.5	18.4
30	2.6	5.4	22.0
35	3.0	6.3	25.7
40	3.4	7.2	29.4
45	3.9	8.1	33.0
50	4.3	9.0	36.7
55	4.7	9.9	40.4

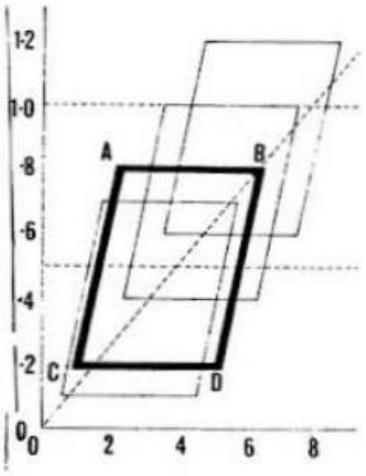
EXPERIMENT NO.9 THE BARIUM-ALKALINE SET

Corner Glazes — The limits of the experiment:

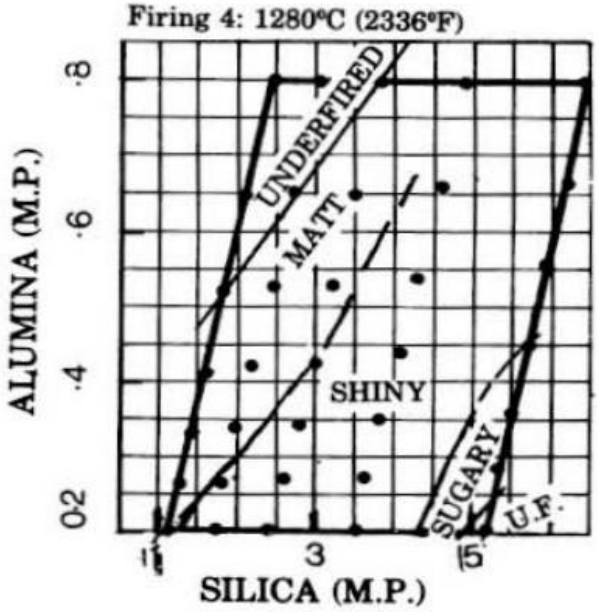
	RECIPE (%)					OXIDE WT. (%)					M.P.
CORNER GLAZES	LITHIUM CARB.	POTASH FELD-SPAR	BARIUM CARB.	KAOLIN	SILICA	Li_2O	K_2O	BaO	Al_2O_3	SiO_2	FLUXES: 0.2 K_2O 0.3 Li_2O 0.5 BaO
											Al_2O_3/SiO_2:
A	5.73	28.76	25.50	40.01	0	2.72	5.71	23.22	24.68	43.67	0.8/2.4
B	3.53	17.74	15.73	24.68	38.32	1.57	3.30	13.44	14.28	67.40	0.8/6.4
C	9.55	47.94	42.51	0	0	4.55	9.57	38.93	10.34	36.60	0.2/1.2
D	4.69	23.55	20.89	0	50.87	2.05	4.31	17.53	4.66	71.44	0.2/5.2

See 'Preliminary Comments on Experiments' (Chapter 8) for experimental details including explanation of data and charts presented here.

Grid Location Diagram:



Results Charts:



BARIUM-ALKALINE SET

Comments on Results

See diagrams opposite.

This set was designed to give alkaline results over a wide range of alumina and silica values without using frits. The K(Na)O and the Li_2O are proper alkalis, and the BaO has some alkaline characteristics. However, the nature of this set is dominated by the BaO, and in many ways it is very like the Barium Set, especially as regards glaze surface, opacity, glaze maturity and response with colouring oxides. It is far more prone to discolouration, however, and development of matt pinks than the Barium Set, when fired in strong reduction. This tendency to discolour in strong reduction is common in highly alkaline glazes. Also, comparison of this set with the Barium Set indicates that Li_2O is far more volatile than the CaO it replaces; the BaO and Li_2O content make this set by far the most volatile of the 8 sets studied.

DATA SHEET — BARIUM-ALKALINE SET

RECIPE (%)

GLAZE No.	Li_2CO_3	K FEL	$BaCO_3$	KAOLIN	SILICA
1	5.73	28.76	25.50	40.01	.00
2	5.18	26.01	23.06	36.18	9.58
3	4.63	23.25	20.62	32.35	19.16
4	4.08	20.50	18.17	28.51	28.74
5	3.53	17.74	15.73	24.68	38.32
6	6.37	31.96	28.34	33.34	.00
7	5.71	28.64	25.40	30.15	10.10
8	5.05	25.33	22.46	26.95	20.21
9	4.38	22.02	19.53	23.76	30.31
10	3.72	18.71	16.59	20.57	40.41
11	7.00	35.15	31.17	26.67	.00
12	6.23	31.28	27.74	24.12	10.63
13	5.46	27.42	24.31	21.56	21.25
14	4.69	23.55	20.88	19.01	31.88
15	3.92	19.68	17.45	16.45	42.50
16	7.64	38.35	34.01	20.01	.00
17	6.76	33.92	30.08	18.09	11.15
18	5.88	29.50	26.16	16.17	22.30
19	4.99	25.07	22.23	14.26	33.45
20	4.11	20.65	18.31	12.34	44.60
21	8.28	41.55	36.84	13.34	.00
22	7.28	36.56	32.42	12.06	11.67
23	6.29	31.58	28.01	10.78	23.34
24	5.30	26.60	23.59	9.50	35.02
25	4.30	21.61	19.17	8.23	46.69
26	8.91	44.74	39.68	6.67	.00
27	7.81	39.20	34.76	6.03	12.19
28	6.71	33.66	29.85	5.39	24.39
29	5.60	28.12	24.94	4.75	36.58
30	4.50	22.58	20.03	4.11	48.78
31	9.55	47.94	42.51	.00	.00
32	8.34	41.84	37.11	.00	12.72
33	7.12	35.75	31.70	.00	25.44
34	5.91	29.65	26.30	.00	38.15
35	4.69	23.55	20.89	.00	50.87

OXIDE WEIGHTS (%)

GLAZE No.	Li_2O	K_2O	BaO	Al_2O_3	SiO_2
1	2.72	5.71	23.22	24.68	43.67
2	2.43	5.11	20.78	22.08	49.60
3	2.15	4.51	18.33	19.48	55.54
4	1.86	3.90	15.89	16.88	61.47
5	1.57	3.30	13.44	14.28	67.40
6	3.03	6.35	25.84	22.29	42.49
7	2.68	5.63	22.91	19.89	48.89
8	2.34	4.91	19.98	17.48	55.28
9	1.99	4.19	17.05	15.08	61.68
10	1.65	3.47	14.12	12.68	68.07
11	3.33	7.00	28.46	19.90	41.31
12	2.93	6.16	25.04	17.69	48.17
13	2.53	5.32	21.63	15.49	55.03
14	2.13	4.48	18.22	13.28	61.89
15	1.73	3.64	14.80	11.07	68.75
16	3.64	7.64	31.08	17.51	40.14
17	3.18	6.68	27.18	15.50	47.46
18	2.72	5.72	23.28	13.49	54.78
19	2.27	4.76	19.38	11.48	62.10
20	1.81	3.81	15.49	9.47	69.42
21	3.94	8.28	33.69	15.12	38.96
22	3.43	7.21	29.31	13.31	46.74
23	2.92	6.13	24.93	11.49	54.53
24	2.40	5.05	20.55	9.68	62.31
25	1.89	3.97	16.17	7.87	70.09
26	4.25	8.93	36.31	12.73	37.78
27	3.68	7.73	31.45	11.11	46.03
28	3.11	6.53	26.58	9.50	54.27
29	2.54	5.34	21.71	7.88	62.52
30	1.97	4.14	16.85	6.26	70.77
31	4.55	9.57	38.93	10.34	36.60
32	3.93	8.26	33.58	8.92	45.31
33	3.30	6.94	28.23	7.50	54.02
34	2.68	5.63	22.88	6.08	62.73
35	2.05	4.31	17.53	4.66	71.44

M.P.

Alumina/Silica (M.P.) Figures same as for the 0.8 Limestone Set

12 DESIGNING AN EXPERIMENT

EXPERIMENT NO.10 DESIGN YOUR OWN BASE GLAZE EXPERIMENT

The final experiment in Part I involves your selecting a set of fluxes and preparing a set of glazes as we have done previously. Obviously the fluxes we have been using can be mixed in an infinite number of combinations; the ones we have used so far were chosen as being fairly representative of a certain type of glaze, limestone glaze, barium glaze etc. The following suggestions may help:

1. You might like to choose fluxes that are intermediate between sets already done in the hope of combining desirable characteristics or simply getting an intermediate blend of results, e.g.

Blend:	**Magnesium and Barium Sets**	**Magnesium and Zinc Sets**	**Zinc and Barium Sets**
	0.2 KNaO	0.2 KNaO	0.2 KNaO
	0.3 CaO	0.3 CaO	0.3 CaO
	0.25 MgO	0.25 MgO	0.25 ZnO
	0.25 BaO	0.25 ZnO	0.25 BaO

Blend:	**Lime/Alkaline Set and Magnesium Set**	**Lime/Alkaline Set and Barium Set**	**Lime/Alkaline Set and Zinc Set**
	0.5 KNaO	0.5 KNaO	0.5 KNaO
	0.3 CaO	0.3 CaO	0.3 CaO
	0.2 MgO	0.2 BaO	0.2 ZnO

and many others.

2. You might like to try a bit of everything!
   e.g.

0.2 KNaO		0.2 KNaO	
0.2 CaO		0.5 CaO	
0.2 MgO	or	0.1 MgO	etc.
0.2 BaO		0.1 BaO	
0.2 ZnO		0.1 ZnO	

3. You may wish to take some particular type of glaze that impressed you from the previous experiments, and see if you can improve on the quality by adjusting the fluxes. For example, if you found the magnesia glazes interesting, you might like to try some of the following adjustments:

0.2 KNaO	0.3 KNaO	0.4 KNaO	
0.4 CaO	0.4 CaO	0.3 CaO	
0.4 MgO	0.3 MgO	0.3 MgO	
0.2 KNaO	0.2 KNaO	0.2 KNaO	0.1 KNaO
0.4 CaO	0.4 CaO	0.3 CaO	0.4 CaO
0.3 MgO	0.3 MgO	0.3 MgO	0.3 MgO
0.1 ZnO	0.1 BaO	0.1 BaO	0.2 ZnO
		0.1 ZnO	etc.

4. If you have a glaze that you use and would like to explore, you could calculate its Seger formula, as explained in Chapter 14, and devise an alumina/silica variation experiment using the same fluxes, but varying Al_2O_3 and SiO_2 around the calculated value for the glaze. Choose your own limits for alumina and silica.

5. You may wish to do something more radical such as having a zero alkali glaze, e.g.

0.4 CaO	0.4 CaO	0.3 CaO
0.3 MgO	0.3 MgO	0.3 MgO
0.3 BaO	0.3 ZnO	0.3 ZnO
		0.1 BaO

or a glaze very high in BaO, ZnO, or MgO, e.g.

0.3 KNaO	0.3 KNaO	0.3 KNaO
0.7 BaO	0.7 MgO	0.7 ZnO

You can expect strange things to happen with such glazes, though it is through probing the limits like this that we discover interesting things.
The possibilities are endless.

Note: If you wish to have a high alkali content but a lower minimum for alumina and/or silica than is possible using feldspar, you can do one of the following:

a. Use an alkaline frit.
b. Use lithium carbonate. (Bear in mind that Li_2O can cause shelling if used in large amounts, e.g. 0.4 M.P., especially in high alumina glazes.)
c. Use nepheline syenite instead of feldspar to get lower minimum silica values.

13 PHASE EQUILIBRIA DIAGRAMS and EUTECTICS

SIMPLE PHASE EQUILIBRIA DIAGRAMS

Most of the materials we use in ceramics are crystalline materials that melt (that is, they change from solid phase to liquid phase) when heated above a certain temperature, known as the melting point (See Diagram 13.1)

This relationship between temperature and phase is fairly simple where we are dealing with pure crystalline materials, and in this case, the actual melting point is the only temperature at which liquid and solid phases can exist together in equilibrium. However, once you mix two or more different crystalline materials together, some very interesting things happen, both to the melting point of the mixture, and to the phase conditions at various temperatures. To examine what happens, let us use a graphical format with a line blend (between A and B) plotted against our temperature scale (A and B are two different crystalline materials). See Diagram 13.2.

If you heat up material A by itself, it will melt at T_a.

If you heat up material B by itself, it will melt at T_b.

If you heat up a mixture of A and B, the melting point will be as indicated on the graph by the Liquidus Line. (Note that all possible mixtures of A and B are catered for in the line blend.)

In this example, the mixture 40A plus 60B has the lowest melting point. This 40/60 mixture is called the 'eutectic composition', and the temperature at which it melts, T_e, is called the 'eutectic temperature' for the A-B system. A few things worthy of note:

T_e is always lower than both T_a and T_b.

T_e is the lowest temperature at which liquid can form in the A-B system, and the interesting thing is that for *any* mixture of A-B, *some* liquid starts to form in the mix

DIAGRAM 13.1 : Temperature Scale

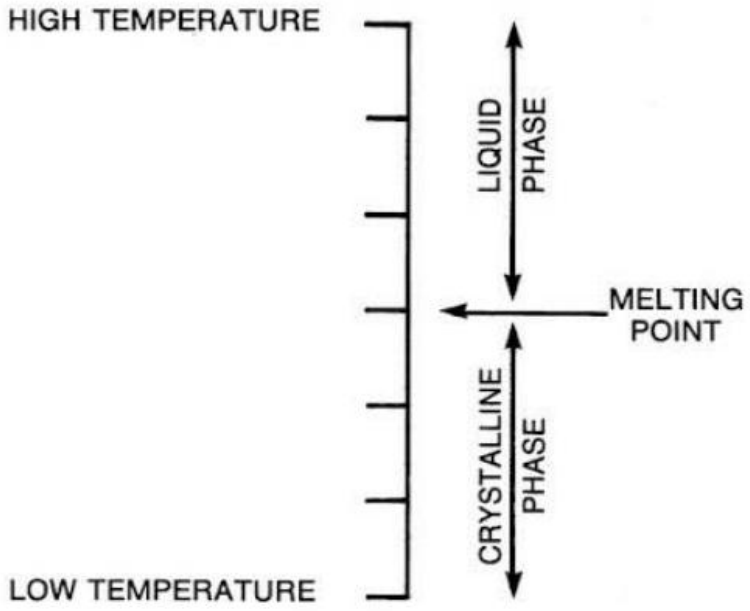
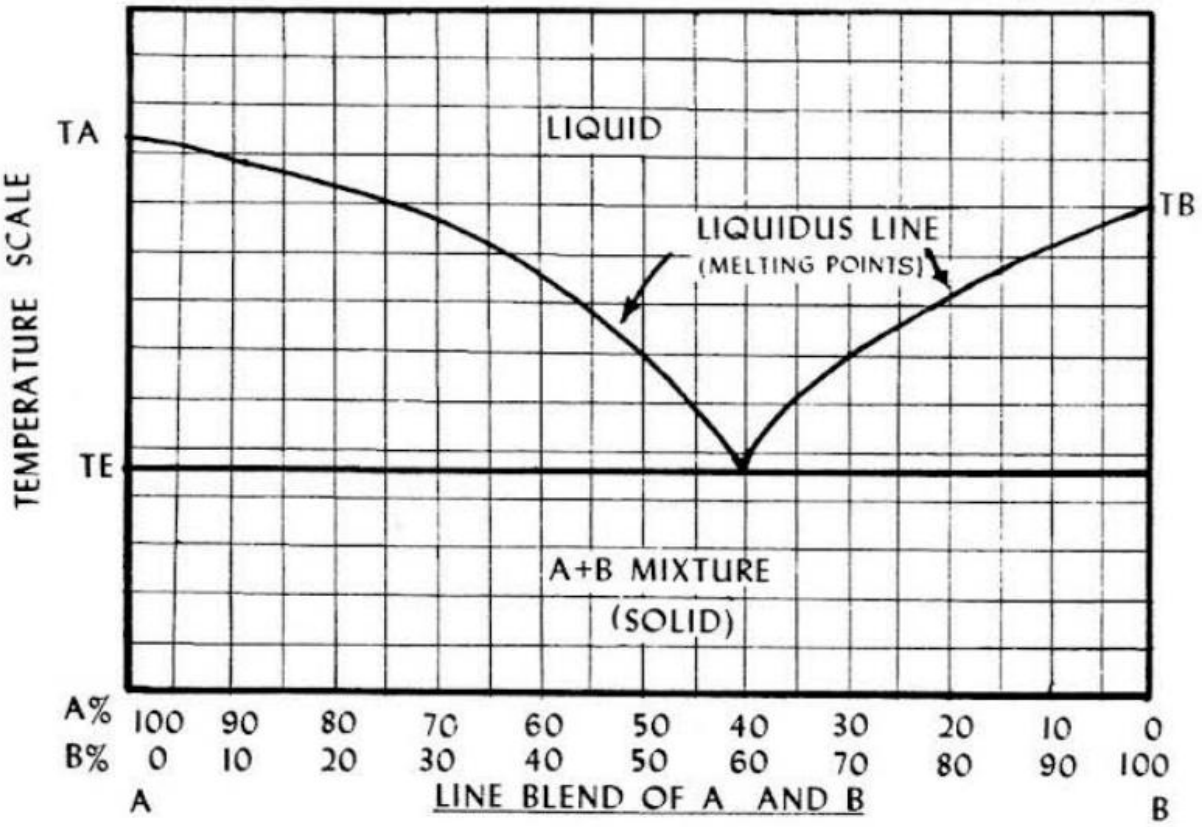
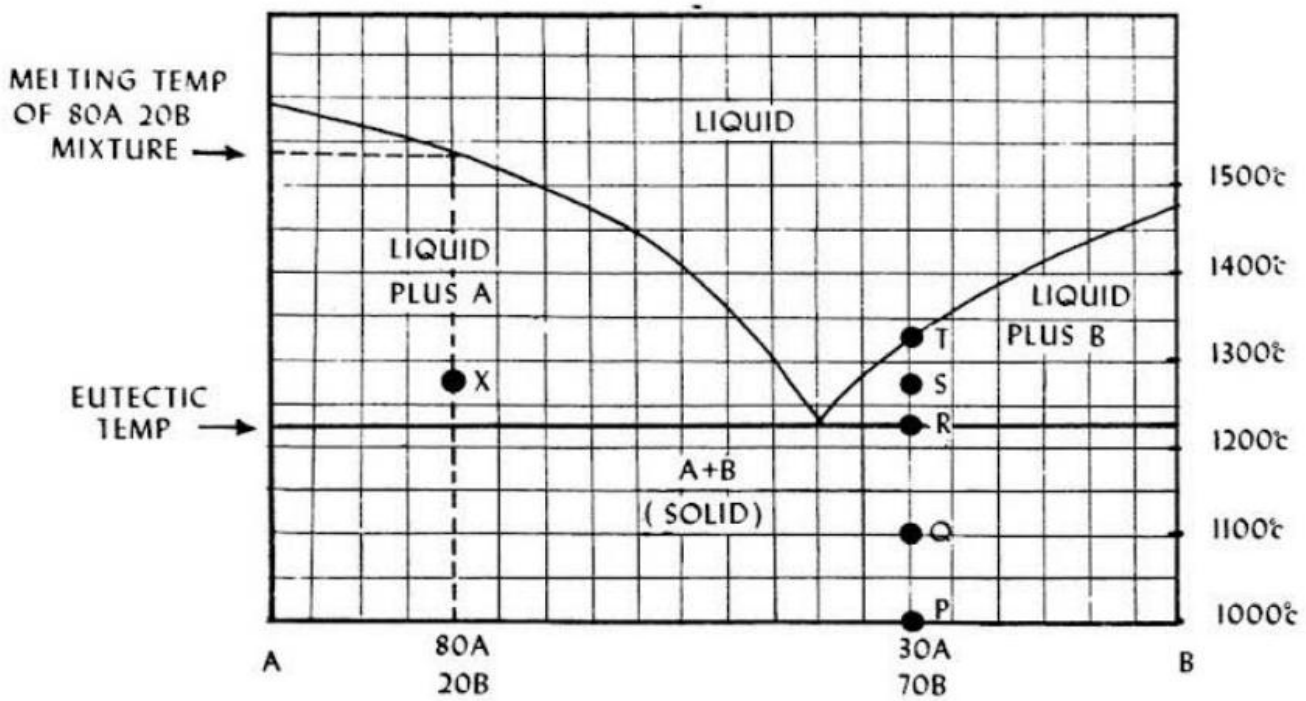


DIAGRAM 13.2: Melting Points of Mixtures of A and B



as soon as the eutectic temperature is reached. In fact, once equilibrium has been reached in any mix that has been heated above T_e, but below its melting point as indicated by the liquidus line, the mixture will consist of liquid plus either pure A or pure B (depending on which side of the eutectic composition the mixture is located). See Diagram 13.3.

DIAGRAM 13.3 : Phase Equilibrium Diagram for Two Materials, A and B



Now . . . why is there liquid phase present in any and all of the blends once T_e is reached? Let us consider the mixture 80A/20B (see again Diagram 13.3): On this side of the eutectic mixture, there is excess of A — in fact we can think of the 80/20 mix as being the eutectic mixture with some extra A thrown in. If you work it out, it comes to 33.3 parts of eutectic mixture plus 66.6 parts or A. Because of the random nature of a mixture, there will be microscopic spots of eutectic mixture that will start to melt as soon as the eutectic temperature is reached. These molten spots grow with time until equilibrium is reached for that temperature. This will occur when all the B is taken into molten solution and only some A is left in solid phase. (This is reversed of course if there is an excess of B in the mixture.) As the temperature rises between the eutectic temperature and the melting point for this mixture, more and more A can be taken into molten solution until at the melting point all A (with time) can enter the liquid phase, and the mixture is 'melted'.

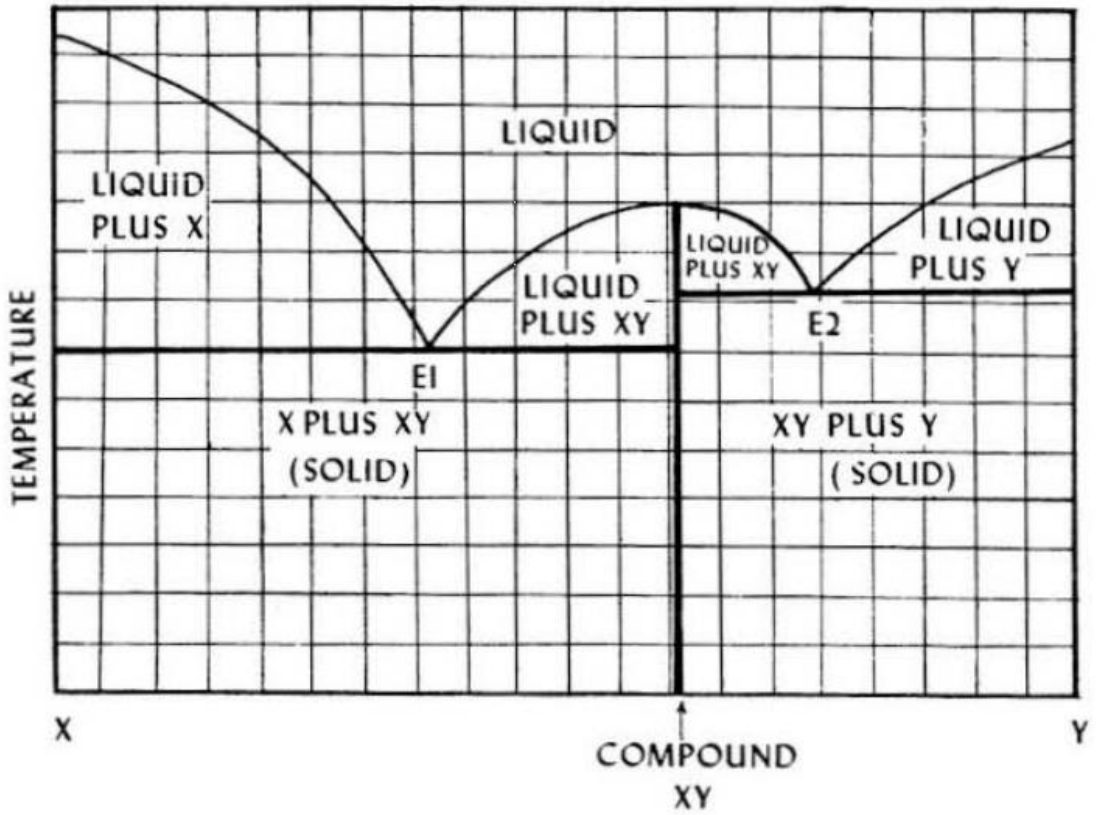
To clarify this further, let us consider a 30/70 mix of A and B (Diagram 13.3):

The point P represents the mixture 30A plus 70B at 1000°C. As the temperature rises to Q (1100°C) not much happens as you are still in the region where A and B are solids. When the temperature reaches R, the eutectic temperature, the point has been reached where liquid is just beginning to form. As temperature continues to rise, you will find at S your mixture now consists of some solid B, plus liquid that is a mixture of A and B, but *no* solid A. At temperature T, the last vestiges of solid B disappear, and all is liquid. The mixture has melted.

Diagram 13.3 is a simple 'Phase Equilibrium Diagram'. From this it is quite simple to pick out the melting temperature for any mixture of A and B, the mixture with the lowest melting point (the eutectic), and the temperature at which liquid (glass) formation first occurs. These are all points of vital interest to the potter.

Just a slight complication to add to this simple picture. These are *Equilibrium* Diagrams. This implies that the temperature is maintained long enough for the liquid to form in the proportions indicated by the diagram. Thus, *time* is an important factor in the attainment of equilibrium.

DIAGRAM 13.4 : P.E. Diagram for Two Materials, X and Y which combine to form the stable compound 'XY'



In many cases where two components X and Y are mixed together and heated, you get compound XY formed, which is relatively stable, compared to mixes on either side of it so that it melts at a higher temperature than mixes on either side. See Diagram 13.4.

Therefore on the line blend from X to Y, there are in this case two eutectics, at E_1 and E_2.

MORE COMPLICATED P.E. DIAGRAMS — TRIAXIAL DIAGRAMS

But these so far have been just two component systems - A and B or X and Y. Glazes usually consist of at least three basic components: fluxes, alumina and silica. So we need a method to examine phase euqilibria for three components. For this we use the triaxial diagram, which allows us to display all possible combinations of three components, as shown (see Diagram 13.5):

Any point within the triangle represents some mix of $CaO/Al_2O_3/SiO_2$.

Any point along the sides of the triangle represents a mix of the two relevant materials.

All possible mixes are catered for as long as the units are % parts by weight.

To work out how much silica there is in a particular mix, relate the point to the silica percentage gradient (which is written in, in Diagram 13.5). For example, any point occurring along line X-X' has 60% SiO_2. Once the gradients for CaO and Al_2O_3 are also drawn in, it is possible to work out their percentages a well. For example, Point A on Diagram 13.5 contains 30% CaO, 10% Al_2O_3, and 60% SiO_2.

See also the text by Fraser for a little on triaxial diagrams. (Ref. 2, page 104)

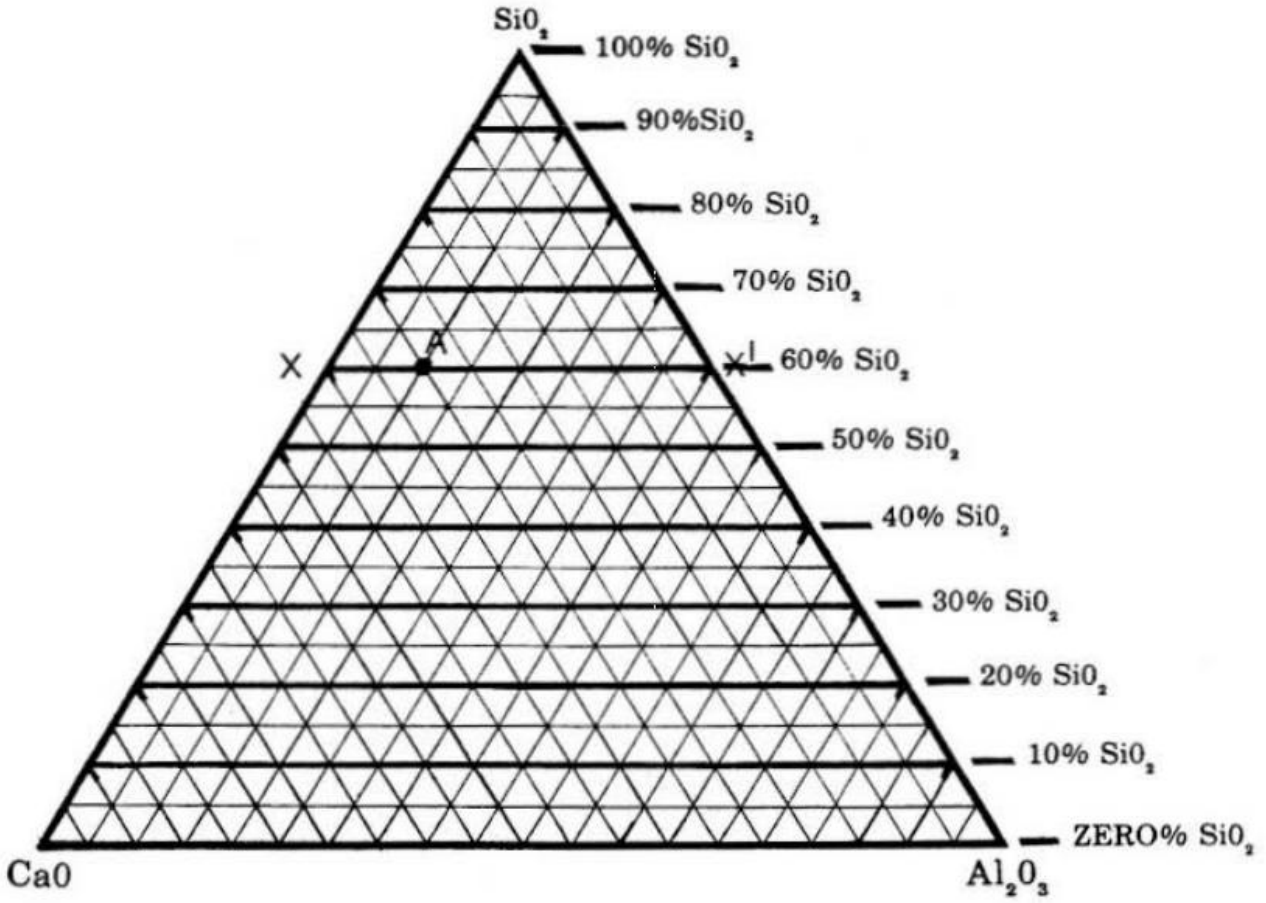
THE EFFECT OF INCREASING THE NUMBER OF INGREDIENTS

Let us consider four pure ingredients, which when fired together will make up a simple limestone glaze:

SiO_2 (melting point — 1720°C)
Al_2O_3 (melting point — 2040°C)
CaO (melting point — 2570°C)
K_2O (melting point red heat)

If we start with the alumina and silica alone, we will find they produce a eutectic at 5.5% Al_2O_3 + 94.5% SiO_2, with a melt-

DIAGRAM 13.5 : Triaxial Diagram — A Percentage Blend of Three Components



ing point of 1595°C. Thus there is a drop of 117°C. below the melting point of pure silica. (See Point 1 in Diagram 13.6. Also, for a full Al_2O_3/SiO_2 phase equilibrium diagram, see Cardew's *Pioneer Pottery*, page 157.)

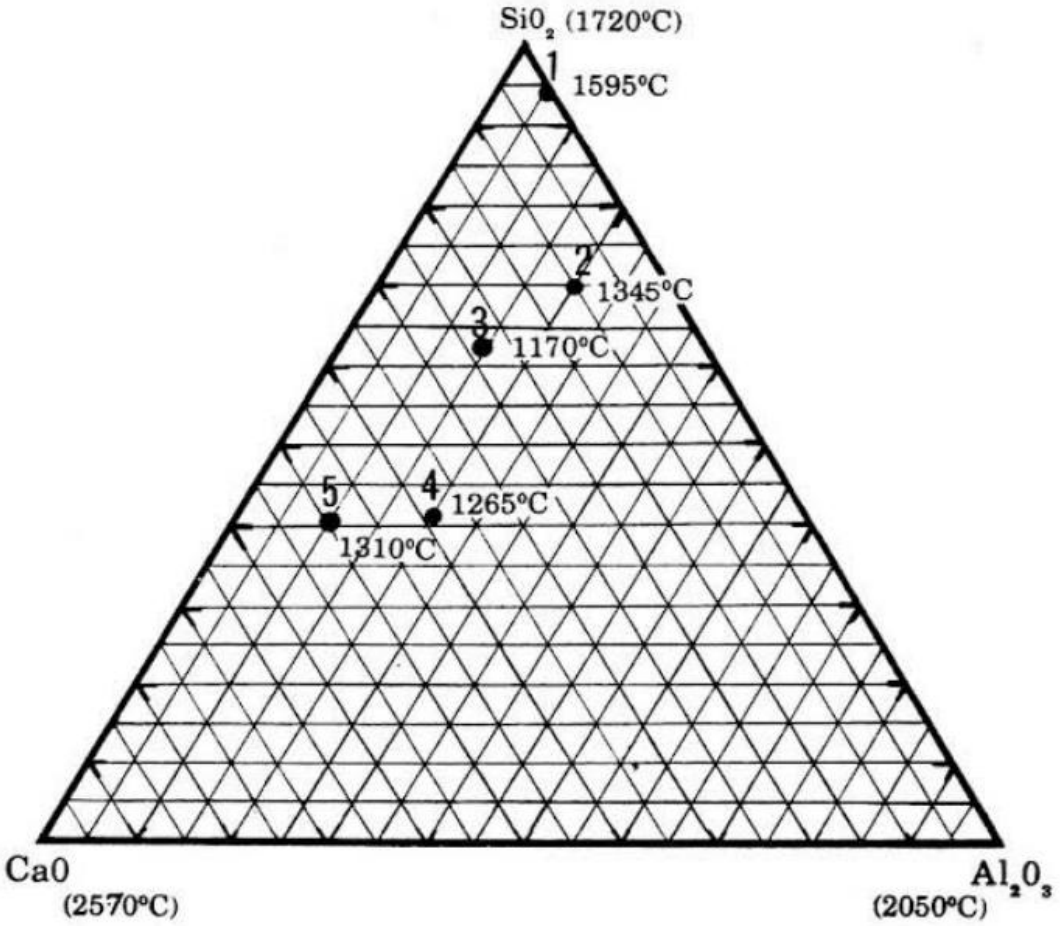
If you add CaO to the above system, many eutectics now appear, the lowest melting point being 1170°C with the formula:

$CaO.0{\cdot}348Al_2O_3.2{\cdot}49SiO_2$.

Expressed as a %, it can be plotted on the triaxial diagram: 23.3% CaO, 14.7% Al_2O_3, 62.2% SiO_2. (See Diagram 13.6, Point 3). Thus the addition of CaO has enabled us to produce a glaze as low as 1170°C, which is 425°C below the Al_2O_3/SiO_2 eutectic. Note also Points 2, 4 and 5, which are other useful eutectics in the $CaO/Al_2O_3/SiO_2$ system.

By adding K_2O to the above, the new four component system has a lowest melting point at 950°C (a drop of 220°C

DIAGRAM 13.6 : Some Eutectic Points in the CaO – Al_2O_3 – SiO_2 System



Eutectics	Composition: % by weight			Melting Points (°C)
	CaO	Al_2O_3	SiO_2	
1	—	5.5	94.5	1595
2	9.8	19.8	70.4	1345
3	23.3	14.7	62.2	1170
4	38.0	20.0	42.0	1265
5	47.2	11.8	41.0	1310

below the previous lowest) and the composition of this eutectic is:

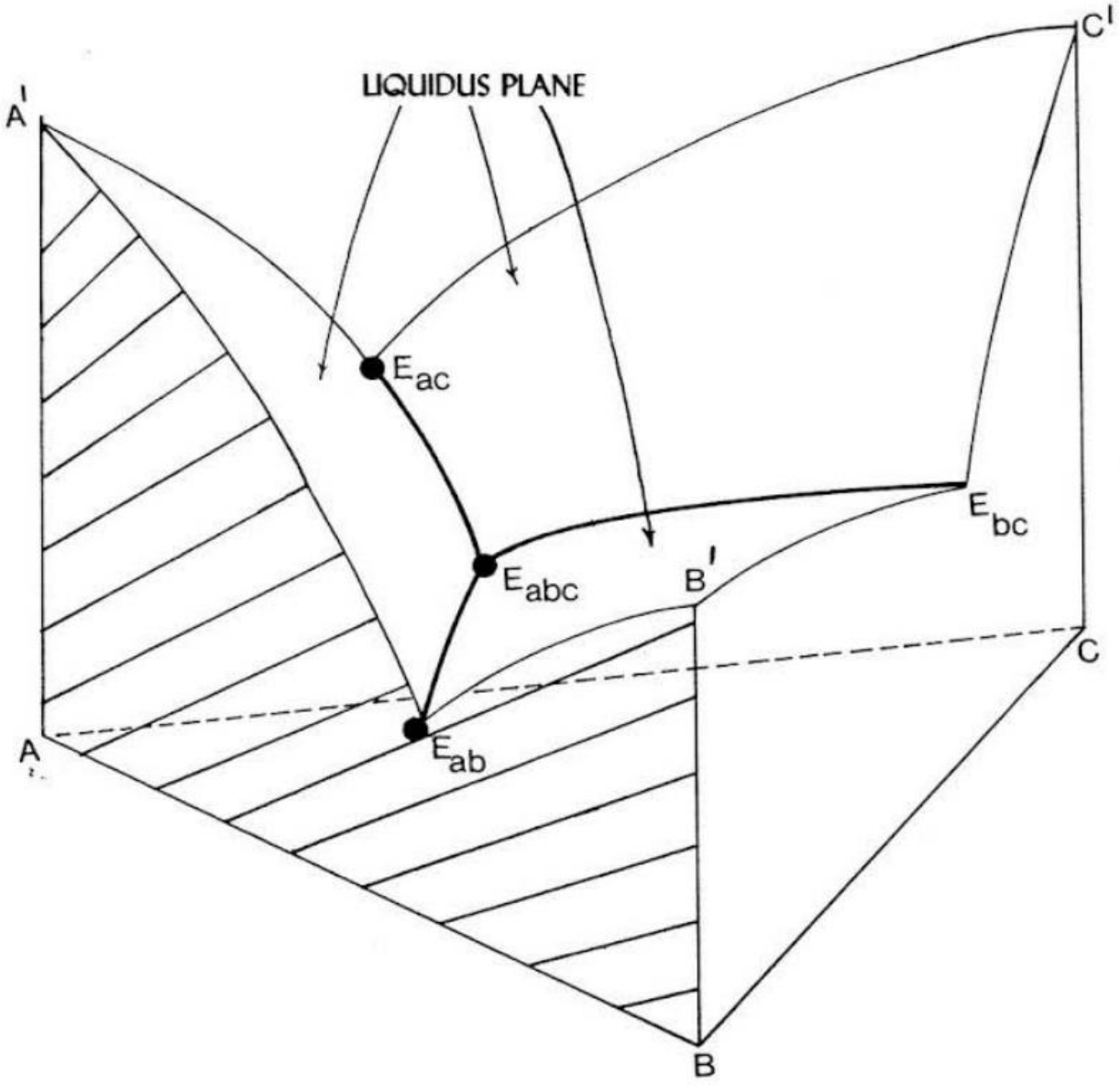
$$\begin{matrix} 0.94\ K_2O \\ 0.06\ CaO \end{matrix} \qquad 0.94\ Al_2O_3\ 11.87\ SiO_2$$

Now that we have four variables, it is no longer possible to draw an appropriate phase diagram on flat paper (unless we use a series of triaxial diagrams); however, we do not need to go that far. The important thing to note is that, every time we add a new oxide to the system, a whole new dimension is added to the phase diagram; a whole new set of eutectics appears, and at least one of these new eutectics will have a lower melting point than the previous lowest. So as you keep adding more and more different oxides, you make possible lower and lower melting points as long as you can find the eutectic compositions.

READING TRIAXIAL PHASE DIAGRAMS

When drawing phase diagrams, we are limited to two dimensions, i.e. the length and breadth of a piece of paper. In the earlier phase diagrams in this Chapter, we plotted two reciprocally variable components (i.e. as one increased, the other decreased by the same percentage) along one axis, and temperature along the other axis. When we draw a triaxial diagram, however, both dimensions of the piece of paper are taken up in recording the *three* reciprocal variables, and we somehow have to superimpose tempera-

DIAGRAM 13.7 : Visualising a Triaxial Diagram in Three Dimensions

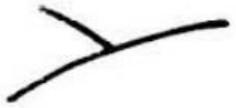


ture data on top of this. The way this is done is by plotting isotherms (i.e. lines joining mixtures of the same melting point, just as contour lines join points of the same altitude on a map) and also by drawing in the eutectic 'troughs' intersecting the isotherms.

Of course, if we were able to draw in three dimensions, it would be possible to draw in the liquidus *plane*, the eutectic 'troughs' or lines etc., corresponding to the liquidus *line* and eutectic temperature points in the two component system.

Diagram 13.7 is an attempt to draw a perspective view of a three-dimensional phase diagram, with the base figure (ABC) representing a triaxial diagram, and the 'vertical' dimension (e.g. AA', BB', CC') representing temperature. The shaded area represents the phase diagram shown in Diagram 13.2. To get from this picture to the normal triaxial phase diagram, imagine that you are looking vertically down on the triaxial diagram in Diagram 13.7 and that you are looking at the liquidus plane. It would look something like Diagram 13.8 showing the three intersecting eutectic 'troughs' joining at the point E_{abc}. (Note that E_{abc} will be a lower temperature than E_{ab}, E_{bc}, or E_{ac}.) If you were to plot onto Diagram 13.8 all the mixes that melt at, say, 1000°C, you might end up with the dotted line. This is the 1000° isotherm.

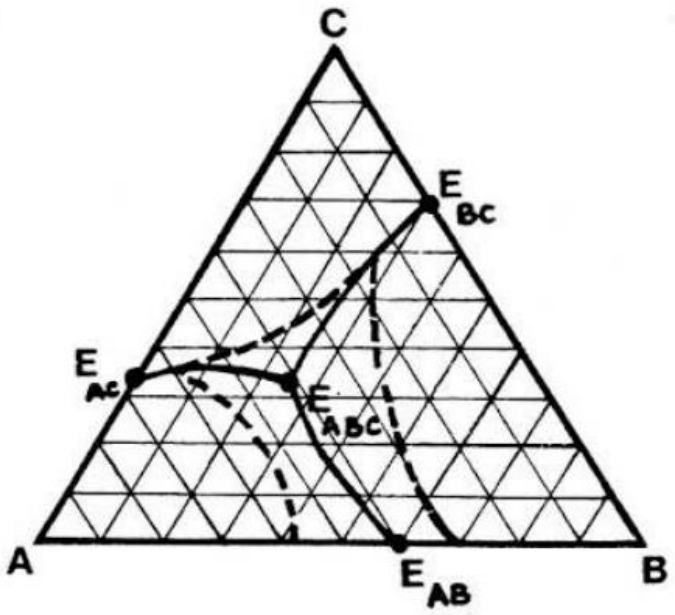
When trying to interpret a triaxial phase diagram, look first for the eutectic trough lines. These will be easy to spot, because here and there they will come together like this:



to give a 'eutectic', or eutectic point (corresponding to point E_{abc} in Diagram 13.8). Secondly, look at the isotherms. These are like contour lines, and should not intersect, though they may come very close together. Somewhere on the isotherms the temperature (melting point) will be printed. Thirdly, look at the relatively stable compounds (corresponding to chemical compound XY in Diagram 13.4) plotted on the diagram, e.g. $CaO.SiO_2$ or $CaO.Al_2O_3.2SiO_2$ etc.

These stable compounds are high temperature peaks on the liquidus plane and occur here and there between the (low temperature) eutectics.

DIAGRAM 13.8 :



SUMMARY

In the glaze tests we have been doing in this course, the limits of alumina and silica have been chosen so that they cover the main eutectic trough and incorporate most of the glazes useful for stoneware in the particular set of glazes being studied.

You should be able to understand now why, for example, just adding a refractory material to a glaze does not necessarily raise the melting point, and adding more fluxes does not necessarily lower it. It depends which side of the eutectic you are on, and whether the addition is going to move you closer to or further from the eutectic. A eutectic represents a delicate balance of all the ingredients in a system. If you have a eutectic mixture, increasing *or* decreasing *any* of the ingredients is going to raise the melting point because *any* alteration is going to upset the balance of the eutectic mixture and move the mixture away from the eutectic to an area of higher melting point.

You should be able to understand how substituting ball clay for China clay, gram for gram in a glaze recipe of, say, an alumina matt glaze, will probably lower the melting point and turn it shiny. Doing the same thing to a high silica opaque glaze will probably give you an underfired glaze, even though ball clay contains some fluxes that are usually absent from the China clay. When you substitute ball

clay for China clay in this way, you are increasing the silica and the fluxes and decreasing the alumina. So referring this to an alumina silica diagram, substituting ball clay for China clay gram for gram will move the glaze down on the chart (less alumina) and to the right (more silica). Also, any significant increase in fluxes will move the glaze towards the zero alumina/silica corner.

It should also now be evident why the presence of very small amounts of impurities in an otherwise refractory mix will cause weakness in that refractory. If the refractory mix has several oxide impurities, even in very small amounts, these will probably mean that the eutectic temperatures for that system are quite low. Therefore, even though the actual mix is well removed from any of the eutectic compositions, small amounts of liquid (glass) are formed as soon as the eutectic temperature is reached. These minute pockets of molten glass in the refractory mix may cause it to weaken and bend under load, long before there is any chance of it melting.

You should also now be able to see how simply diversifying the fluxes will usually lower the melting point of a glaze. For example, if you want to lower the melting point of one of the limestone glazes without changing other characteristics significantly, you could try substituting other fluxes for some of the CaO, e.g. 0.1 M.P. of ZnO, BaO, Li_2O or MgO, or a combination of these. By diversifying the fluxes, you are increasing the number of eutectics in the system; and other factors remaining constant, you will usually find that the glaze now matures at a lower temperature.

REFERENCES

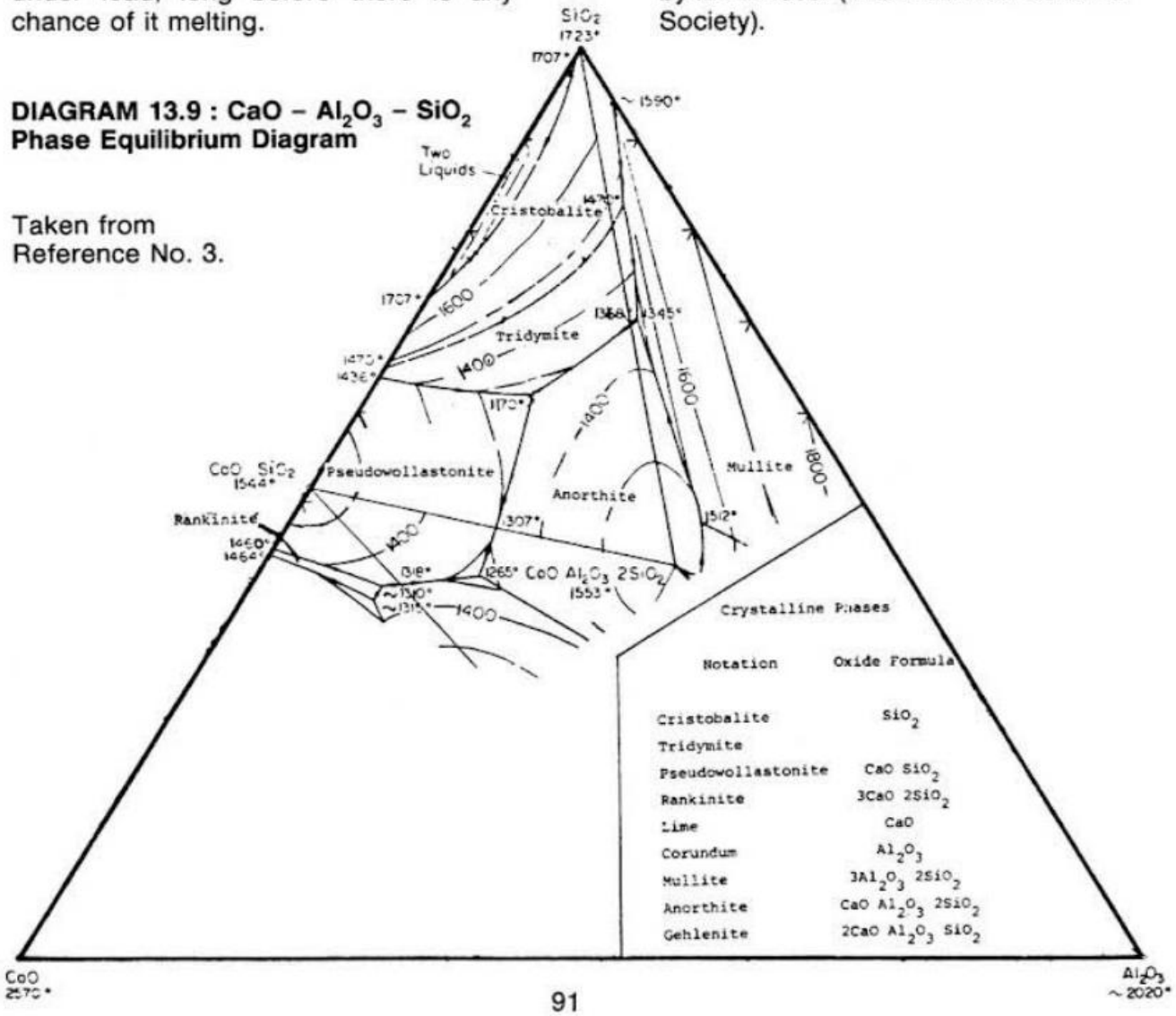
1. Chapter 17 in *Ceramic Science for the Potter* by W.G. Lawrence (Chilton).

2. *Glazes for the Craft Potter* by Harry Fraser (Pitman).

3. *Phase Diagrams for Ceramists* by Levins, Robbins and McMurdie, Edited by M.K. Reser (The American Ceramic Society).

DIAGRAM 13.9 : CaO – Al_2O_3 – SiO_2
Phase Equilibrium Diagram

Taken from
Reference No. 3.



14 CALCULATIONS

If unfamiliar with basic chemistry, you should read Chapter 2 before starting this chapter.

CONVERTING FORMULA TO RECIPE

This follows on directly from the example for anorthite given at the end of Chapter 2, showing how we systematise the calculation process using a conversion chart.

Using a Conversion Chart

We use a conversion chart to simplify the process of converting a molecular formula or Seger formula to a recipe. Look at the chart (Conversion Chart No.1) and have at hand Table 14.1 ('List of Raw Material'). (See Page 96.)

Note that the chart divides into two halves - the left-hand side represents the *raw materials before* firing, and the right-hand side represents *the oxides after* the firing, i.e. the raw materials on the L.H.S. provide the oxides for the R.H.S.

The first thing we do is write down the oxides and amounts required (molecular parts) at the tops of Columns 6, 7, 8 underneath 'Required Glaze'. We are going to do the anorthite problem again, so we write in '1 CaO' '1 Al_2O_3' '$2SiO_2$' respectively at the tops of Columns 6, 7 and 8.

Order of Calculation

Because some ingredients add more than one oxide to the glaze, it is necessary to do the calculation in a certain order to prevent overloading. The order suggested by Nigel Wood in his book, *Oriental Glazes*, (Pitman) is as follows:

$K_2O + Na_2O$, Al_2O_3, MgO, P_2O_5, CaO, SiO_2, Fe_2O_3.

This order may need to be changed for certain glazes, or if using certain raw materials. If using a pure kaolin or alumina itself as your 'top-up' source of alumina, you can leave it until just before the silica. However, if using less pure clay, the alumina should be dealt with immediately after the K_2O and Na_2O. The order I will use in this course, based on that suggested by Nigel Wood will usually be:

K_2O, Na_2O, Al_2O_3, MgO, CaO, BaO, ZnO, SiO_2

It this does not make much sense at this time, do not worry — you will get the feel for it automatically as you get practice at the calculations.

Four Question Technique

Having decided to start with alumina, there are four questions we ask in order to fill in the first line:

Alumina

Question 1:

How much Al_2O_3 do we need to provide?
(see 'Required Glaze').

Answer:
1 Molecular Part
Entry:
Enter '1' in column 7.

Question 2:
What raw material will we use to provide this 1 M.P. of alumina?
(See Table 14.1).
Answer:
Kaolin. (We could use alumina too).
Entry:
Enter 'kaolin' in Column 1.

Question 3:
How many molecular parts of kaolin are required to give us the required 1 M.P. of alumina?
Answer:
1 M.P. kaolin.
Entry:
Enter '1' in Column 2.

Question 4:
Does this 1 M.P. of kaolin bring any other oxides into the glaze? If so, how much?
Answer:
Yes. It brings 2 M.P. of SiO_2.
Entry:
Enter '2' in Column 8.

The four questions now being completed for alumina, you now look up the molecular weight of kaolin (Table 14.1) and write it in Column 3. Multiply Column 2 by Column 3 to get Column 4.
Leave Column 5 for the time being.

CaO

Now you move onto providing the CaO. You ask yourself the same four questions, but always after the first line entries, Question 1 will be slightly changed as follows:

Question 1:
How much CaO do we still need to provide?
(Equals amount listed in 'Required Glaze' minus any previous entries).

CONVERSION CHART NO. 1

1	2	3	4	5	6	7	8
Raw Material	Molecular Parts	Molecular Weight	Parts by Weight	% Parts by Weight	Required Glaze		
					1.0 CaO	1.0 Al_2O_3	2.0 SiO_2
Kaolin	1	258.1	258.1	72.1		1	2
Whiting	1	100.1	100.1	27.9	1		
		Totals:	358.2	100.0%	1	1	2

This part of the chart relates to the raw materials, i.e. **before** the firing

This part relates to the oxides present **after** the firing.

Answer:

1 M.P. (since there were no previous entries of CaO).

Entry:

Enter '1' in Column 6.

Following the rest of the questions through as before, we decide to use whiting (Column 1), find that we need 1 M.P. of it (Column 2) find that it adds no other oxides to the glaze, look up the molecular weight of whiting (Table 14.1) (enter in Column 3) and multiply Column 2 by Column 3 to give Column 4.

SiO_2

Question 1:

How much SiO_2 do we still need to provide, i.e. 'Required Glaze' (2 M.P.) minus previous entries (2 M.P. from the kaolin)?

Answer:

Zero.

So we have provided all the oxides in the required amounts.

Percentage Calculation

We can use the Parts by Weight in Column 4 as our recipe, or we can convert these numbers into a percentage as follows:

Firstly, add up Column 4 to give 'Total Parts by Weight'

General Formula: % Parts by Weight $= \frac{\text{Parts by Weight x 100}}{\text{Total Parts by Weight}}$

$$\text{Therefore \% kaolin} = \frac{258.1 \times 100}{358.2\ \%} = 72.1\%$$

$$\%\ \text{Whiting} = \frac{101.1 \times 100}{358.2} = 27.9\%$$

FORMULA TO RECIPE CONVERSION FOR CONE 9 LIMESTONE GLAZE

Having understood the previous section, we should now be able to handle a normal stoneware glaze, such as:

$$\begin{matrix} 0.2\ K_2O \\ 0.8\ CaO \end{matrix} \quad 0.5\ Al_2O_3\ 4.0\ SiO_2$$

This is a clear shiny glaze at Seger cone 9 and can be regarded as a starting point for our experiments in varying fluxes, alumina and silica.

Note that the quantities of some of the oxides are expressed in decimal fractions (e.g. 0.2 K_2O) whereas in the anorthite example, we used only whole numbers. This is no cause for concern. If you were to multiply every number by 10 to give the following formula:

$$\begin{matrix} 2\ K_2O \\ 8\ CaO \end{matrix} \quad 5\ Al_2O_3\ 40\ SiO_2$$

this is exactly the same glaze. The only difference is that if you want to express the glaze in this way, then you will also have to multiply the molecular weight of the glaze by 10.

Unity Formula

It is a convention in glaze formulae that the fluxes add up to unity (0.2 + 0.8 = 1), and as I mentioned previously, since we are often dealing with 'parts of a molecule' (e.g. 0.2) we use the term 'Molecular Parts (M.P.)' rather than 'molecules'.

So let us convert the Seger formula shown above to a percentage recipe. I will explain it in full detail, and you will be able to use the following explanation as a model for doing further conversions.

Seger Formula to Percentage Recipe — Model Conversion

a. Draw up an empty chart as shown (Conversion Chart No.2) with Columns 1 to 9.

b. Insert the names of the oxides required, and the amounts, under the heading 'Required Glaze' i.e. Columns 6 to 9.

c. Determine from the 'Order of Calculation' the order in which we will fill the oxide requirements. The order will be K_2O, Al_2O_3, CaO, SiO_2.

d. We now proceed to filling in the chart one line at a time, using the Four Question Technique, starting with K_2O:

K_2O

Question 1:
How much K_2O do we require, bearing in mind any previous entries (zero in this case)? See Column 6 under 'Required Glaze'.
Answer:
0.2 M.P. K_2O.
Entry:
Enter 0.2 in Column 6.

Question 2:
What raw material will we use to provide this 0.2 M.P. of K_2O? (See Table 14.1).
Answer:
Feldspar. (For any required oxide, there is usually a variety of potential raw materials. You will develop a feeling for the most suitable choice as you get more experience. See also the chapter on 'Raw Materials'. Meanwhile, I will simply indicate to you the material I think you should use.)
Entry:
Enter 'feldspar' in Column 1.

Question 3:
How many molecular parts of feldspar are needed to give us 0.2 M.P. of K_2O?

CONVERSION CHART NO. 2: FORMULA TO RECIPE

1	2	3	4	5	6	7	8	9
Raw Material	Molecular Parts (M.P.)	Molecular Weight	Parts by Weight	% Parts by Weight	Required Glaze			
					0.2 K_2O	0.8 CaO	0.5 Al_2O_3	4 SiO_2
Feldspar	0.2	556.5	111.3		0.2		0.2	1.2
Kaolin	0.3	258.1	77.4				0.3	0.6
Whiting	0.8	100.1	80.1			0.8		
Silica	2.2	60.1	132.2					2.2
Totals:								

Note: One place of decimals in the values listed in Colums 3, 4 and 5 is more than adequate accuracy.

Note: 1 molecule of feldspar

K_2O — 1 molecule of K_2O

Al_2O_3 — 1 molecule of Al_2O_3

$6SiO_2$ — 6 molecules of SiO_2

From this we see that *one* molecule of feldspar gives *one* molecule of K_2O. Therefore, the required 0.2 molecules of K_2O will be provided by 0.2 molecules (M.P.) of feldspar.

Answer:

0.2 M.P. of feldspar.

Entry:

Enter 0.2 in Column 2.

Question 4:

Does this 0.2 M.P. of feldspar bring any other oxides into the glaze (apart from the 0.2 M.P. K_2O already listed in Column 6)? If so, how much?

Answer:

Yes. It brings in alumina and silica as well. Quantities are obvious as follows:

1 molecule feldspar provides:

1 M.P. K_2O, 1 M.P. Al_2O_3, 6 M.P. SiO_2

Therefore, 0.2 M.P. feldspar provides:

0.2 M.P. K_2O, *0.2* M.P. Al_2O_3, *1.2* M.P. SiO_2

(Note: The 1.2 SiO_2 results from 0.2 x 6.)

Entry:

Enter 0.2 in Column 8 (alumina).
Enter 1.2 in Column 9 (silica).

TABLE 14.1: LIST OF RAW MATERIALS

Note: This list contains only materials that are insoluble in water, or largely so. For more complete coverage, see the suggested texts by Fraser or Hamer.

NAME	MOLECULAR FORMULA	MOLECULAR WEIGHT
Alumina	Al_2O_3	101.9
Alumina Hydrate	$Al_2O_3.3H_2O$	156
Barium Carbonate	$BaCO_3$	197.4
Calcium Carbonate	$CaCO_3$	100.1
China clay	$Al_2O_3.2SiO_2.2H_2O$	258.1
Dolomite	$CaCO_3.MgCO_3$	184.4
Feldspar (potash)	$K_2O.Al_2O_3.6SiO_2$	556.5
Feldspar (soda)	$Na_2O.Al_2O_3.6SiO_2$	524.3
Kaolin	$Al_2O_3.2SiO_2.2H_2O$	258.1
Lithium Carbonate	Li_2CO_3	73.9
Magnesium Carbonate	$MgCO_3$	84.3
Silica (Quartz)	SiO_2	60.1
Talc	$3MgO.4SiO_2.H_2O$	379.2
Whiting	(See Calcium Carbonate)	
Zinc Oxide	ZnO	81.4

NOTE: All molecular weights used in this course are as listed in Fraser's text, Appendix 9 or Appendix 10, unless otherwise stated.

You now look up the molecular weight of potash feldspar in Table 14.1 and enter this figure (556.5) in Column 3.

Multiply Column 2 by Column 3 to get Column 4 (111.3)

Al_2O_3

Question 1:

How much Al_2O_3 do we require (bearing in mind any previous entries . . . 0.2 M.P. in this case, entered in Column 8 from the feldspar).

Answer:

0.5 minus 0.2 equals 0.3 M.P.

Entry:

Enter 0.3 in Column 8.

Question 2:

What raw material will we use to provide this 0.3 M.P. Al_2O_3? (Look up sources of Al_2O_3 in Table 14.1. In this case we will use kaolin.)

Answer:

Kaolin.

Entry:

Enter kaolin in Column 1.

Question 3:

How many M.P. of kaolin are needed to provide the required 0.3 M.P. of Al_2O_3?

Answer:

0.3 M.P.

Note:

1 molecule of kaolin

Al_2O_3	$2SiO_2$	$2H_2O$
1 molecule of Al_2O_3	2 molecules of SiO_2	2 molecules of H_2O

(From this it is obvious that one molecule of kaolin provides one molecule of alumina, and it follows that the required 0.3 M.P. of alumina will be provided by 0.3 M.P. of kaolin.)

Entry:

Enter '0.3' in Column 2.

Question 4:

Does this 0.3 M.P. kaolin bring any other oxides into the glaze? If so, how much?

Answer:

Yes. It brings silica. You will see from studying the diagram in the previous Answer that every 1 M.P. alumina will bring with it 2 M.P. silica. Therefore 0.3 M.P. alumina will bring 0.6 M.P. silica. The water (H_2O) burns out.

Entry:

Enter '0.6' in Column 9.

Fill in Column 3 and Column 4 as explained for K_2O.

CaO

Question 1:

How much CaO do we need to provide, bearing in mind any previous entries (zero in this case)?

Answer:

0.8 M.P.

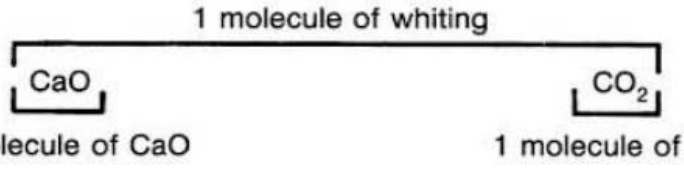
Entry:

Enter '0.8' in Column 7.

Question 2:
What raw material will we use to provide this CaO? (Check Table 14.1. Use whiting.)
Answer:
Whiting.
Entry:
Enter 'whiting' in Column 1.

Question 3:
How many molecular parts of whiting do we need to give 0.8 M.P. CaO?

Note:



1 molecule of CaO is provided by 1 molecule of whiting. Therefore, 0.8 molecules of CaO is provided by 0.8 molecules of whiting.

Answer:
0.8 M.P.
Entry:
Enter '0.8' in Column 2.

Question 4:
Does this whiting bring any other oxides into the glaze? If so, how much?
Answer:
No. The CO_2 burns out.
Fill in Column 3 and Column 4 as explained for K_2O.

SiO_2

Question 1:
How much SiO_2 do we require, bearing in mind previous entries (from feldspar and kaolin).
Answer:
4 M.P. minus 1.2 M.P. minus 0.6 M.P. equals 2.2 M.P.
Entry:
Enter '2.2' in Column 9.

Question 2:
What raw material will we use?
Answer:
Silica.
Entry:
Enter 'silica' in Column 1.

Question 3:
How many M.P. of silica do we need?
Answer:
2.2 M.P.
Entry:
Enter '2.2' in Column 2.

Question 4:
Does this silica bring any other oxides into the glaze?
Answer:
No.

Fill in Column 3 and Column 4 as explained for K_2O.

To check that all the oxide requirements have been met, add up Columns 6, 7, 8 and 9 separately, and enter the results in 'Totals'. These totals must tally with the amounts written under 'Required Glaze'. Do this yourself now, to check.

e. Percentage Calculation

Add up Column 4. In this case, the answer is 401. Insert this in 'Total Parts by Weight'.

The Percentage Formula:

$$\% \text{ Parts by Weight} = \frac{\text{Parts by Weight} \times 100}{\text{Total Parts by Weight}}$$

Therefore:

Feldspar %	=	$\frac{111.3 \times 100}{401}$	=	27.8%
Kaolin %	=	$\frac{77.4 \times 100}{401}$	=	19.3%
Whiting %	=	$\frac{80.1 \times 100}{401}$	=	20.0%
Silica %	=	$\frac{132.2 \times 100}{401}$	=	33.0%
			Total :	100.1%

Total up the percentages to check that they equal 100 (or close to it). Any large error indicates an error either in the 'Parts by Weight' total, or one of the percentage calculations, or your Column 5 total.

Enter the percentages in Column 5. Do this yourself now.

And that is all there is to it. This explanation may seem drawn out, but this method was developed for teaching the procedure by correspondence lessons to students with no previous knowledge of chemistry, and I have tried to cover every possible query.

EXERCISE

Convert the following molecular formulae to recipes, *using the same raw materials* as in the one just done:

(a) $0.2\ K_2O$, $0.8\ CaO$ — $0.8\ Al_2O_3\ 2.4\ SiO_2$

(b) $0.2\ K_2O$, $0.8\ CaO$ — $0.8\ Al_2O_3\ 6.4\ SiO_2$

(c) $0.2\ K_2O$, $0.8\ CaO$ — $0.2\ Al_2O_3\ 1.2\ SiO_2$

(d) $0.2\ K_2O$, $0.8\ CaO$ — $0.2\ Al_2O_3\ 5.2\ SiO_2$

Notice that all four glazes have the same flux content. Only the alumina and silica vary. These glazes are the 'corner glazes' for the 0.8 Limestone set.

CONVERSION OF RECIPE OR ANALYSIS TO SEGER FORMULA

In this section, you will do the reverse of the formula to recipe conversion just done. Often you will find that you have a recipe or analysis (of a glaze or clay or rock etc.) expressed in parts by weight, and you want to know the seger formula. For example, you might want to use the material as a raw material in your glaze calculations, but before you can do this, you must work out the seger formula, and also the molecular weight, unless using the Percentage Method. See P. 107.

In our conversion of formula to recipe, the key process was to convert 'molecular parts' to 'parts by weight' by the following process:

Molecular Parts x Molecular Weight = Parts by Weight

In our present problem, we already have 'Parts by Weight', and we want to get 'Molecular Parts'. To get it, we simply reverse the above process thus:

Parts by Weight ÷ Molecular Weight = Molecular Parts

This is the key calculation in the conversion. All other calculations being simply to get the resulting molecular parts into a standardised form (in the case of a glaze with total fluxes equal to 1.0, and in the case of a clay with Al_2O_3 equal to 1.0). Let us look at a simple example. In Bernard Leach's *A Potter's Book* on page 165, he quotes Hamada as giving the following recipe as a starting point for celadon glazes;

Limestone	1
Quartz	2
Feldspar	3
plus Red Iron Oxide	1%

However, this glaze usually turn out more like a Chun that a celadon. By examining the molecular formula of the glaze, we can get some idea why this is so. Let us do the conversion.

CONVERSION OF A GLAZE RECIPE TO SEGER FORMULA

Firstly, let us regard the red iron oxide as a colouring oxide and simply tack it onto the end of the molecular formula as a percentage. Some authors include their colouring oxides in the molecular formula; and in the case of iron oxide in a glaze fired under reduction, the iron oxide should theoretically be included in the fluxes as FeO (reduced iron oxide) because iron oxide when fired under reduction acts as a flux. I will give an example of this later, but for the time being, I will do the conversion just on the 'base glaze' of limestone, quartz and feldspar.

CONVERSION CHART 3: GLAZE RECIPE TO MOLECULAR FORMULA

1	2	3	4	5	6	7	8
Material	Parts by Wt.	÷ Mol. Wt.	= Mol. Parts	K_2O	CaO	Al_2O_3	SiO_2
Limestone	1	÷ 100	= 0.0100		0.0100		
Quartz	2	÷ 60.1	= 0.0333				0.0333
Feldspar	3	÷ 556	= 0.0054	0.0054		0.0054	0.0324
		Oxide Totals:		0.0054	0.0100	0.0054	0.0657
		Total Fluxes:		0.0154			
Divide each of the oxide totals by 0.0154:				0.35	0.65	0.35	4.27

Columns 1 to 4 are fairly straightforward - for each of the raw materials, you divide the parts by weight (from the recipe) by the molecular weight of that material, to give molecular parts (column 4). But we want molecular parts of simple oxides, and feldspar contains three oxides. So we transfer the figures in column 4 over into the appropriate columns of simple oxides (columns 5 to 8). Note that the 0.0054 M.P. of feldspar provides 0.0054 M.P. of K_2O, plus 0.0054 M.P. of Al_2O_3, plus 0.0324 (= 0.0054 x 6) M.P. of SiO_2. You now add the columns ('Oxide Totals'), and you have a molecular formula thus:

0.0054 K_2O
0.0100 CaO 0.0054 Al_2O_3 0.0657 SiO_2

However, the normal convention is to bring the total fluxes to unity, whereas in this case, K_2O plus CaO equals 0.0154. So we have to get this figure equal to 1.0, without changing the ratio of the oxides, one to another. We do this by dividing all the numbers by the sum of the fluxes (0.0154 in this case). This gives the last line in the conversion chart 3, and so the molecular formula can be written as follows:

0.35 K_2O 0.35 Al_2O_3 4.27 SiO_2
0.65 CaO plus 1% Red Iron Oxide

Examination of this formula allows one to see why it often produces a Chun glaze. When we cover traditional glazes in Part II, you will find this formula fairly typical of a Chun, rather than a celadon glaze, especially as regards the relatively low alumina. Also the alumina/silica ratio, which works out at 1:12.2, is typical.

CONVERSION OF ANALYSIS DATA (%) TO SEGER FORMULA AND MOLECULAR WEIGHT (OXIDE WEIGHT % TO SEGER FORMULA)

I would like to work through another conversion with you to show how to take the analysis data for a raw material and work out the seger formula for this material and its molecular weight. It is basically the same process as the previous example, but the 'recipe' that you start with is the oxide percentages as listed in the analysis. For example, in Russell Cowan's *Technical Notes for the Craft Potter*, the following analysis is given for Ball Clay QA:

SiO_2	57.2%
Al_2O_3	27.0%
TiO_2	1.5%
Fe_2O_3	0.9%
CaO	0.3%
MgO	1.0%
Na_2O	1.0%
K_2O	1.0%
Loss on Ignition	8.4%

The procedure is as follows (see Conversion Chart 4):

a. List the oxides and percentages in columns 1 and 2, according to the analysis. Note: Temporarily ignore the 8.4% L.O.I. (Loss on Ignition). This means that for the time being, the seger formula and molecular weight that we work out are for the fired, or calcined, ball clay QA. Once we have obtained this, we will then make allowance for the 8.4% of weight that is lost in the firing, and thereby obtain the molecular weight of the raw or unfired ball clay.
b. Obtain the molecular weights of the oxides from Appendix 10 in Fraser's text (or other) and insert in column 3.
c. Divide the 'Parts by Weight' (%) by the 'Molecular Weight' to give 'Molecular Parts' (column 4).
d. Column 4 now gives us the molecular parts of the various oxides, and taken as a whole, it gives a molecular formula for the clay. With clays, the convention is to have alumina equal to 1.0 M.P. In column 4 however it equals 0.265. To get the correct seger formula, we divide all the numbers in column 4 by the alumina figure, to give column 5. From column 5 we now read off the molecular formula as follows:

0.04 K_2O
0.06 Na_2O 1.0 Al_2O_3 3.59 SiO_2 Calcined
0.02 CaO 0.02 Fe_2O_3 0.07 TiO_2 Ball Clay QA
0.09 MgO

Note that compared with theoretical kaolin (1.0 Al_2O_3. 2 SiO_2. 2H_2O.), there is a lot more silica, and a significant amount of fluxes (0.10 KNaO, and 0.11 of CaO plus MgO).

CONVERSION CHART 4: ANALYSIS TO MOLECULAR FORMULA AND MOLECULAR WEIGHT

1 Oxide	2 Parts by Weight (%)	3 Molecular Weight	4 Molecular Parts		Alumina M.P.		5 Molecular Parts	6 Molecular Weight	7
SiO_2	57.2	60.1	0.952	÷	0.265	=	3.59	60.1	215.8
Al_2O_3	27.0	101.9	0.265	÷	0.265	=	1.00	101.9	101.9
TiO_2	1.5	79.9	0.019	÷	0.265	=	0.07	79.9	5.6
Fe_2O_3	0.9	159.7	0.006	÷	0.265	=	0.02	159.7	3.2
CaO	0.3	56.1	0.005	÷	0.265	=	0.02	56.1	1.1
MgO	1.0	40.3	0.025	÷	0.265	=	0.09	40.3	3.6
Na_2O	1.0	62.0	0.016	÷	0.265	=	0.06	62.0	3.7
K_2O	1.0	94.2	0.011	÷	0.265	=	0.04	94.2	3.8
L.O.I.	8.4								
							M.Wt Calcined =		338.7

e. If you want to use ball clay QA as a glaze ingredient in your calculations, you will need to know the molecular weight. Proceed as follows:

In column 6, write down (again) the molecular weights of the oxides. Multiply column 5 by column 6 to give column 7. Add up column 7, and the total is the molecular weight of the ball clay after it has been fired. To get the molecular weight of the unfired material, we must make allowance for the water, carbonates, sulphides etc. that burn out. These losses make up 8.4% of the unfired clay weight (see in the analysis, '8.4% Loss on Ignition'). Use the following formula to get the molecular weight of the unfired material:

$$\text{M.Wt of Unfired Material} = \frac{\text{M.Wt of Calcined Material} \times 100}{(100 - \text{L.O.I.})}$$

$$\text{Therefore M.Wt of Raw Ball Clay QA} = \frac{338.7 \times 100}{100 - 8.4}$$

$$= 369.8$$

Incidentally, we do not need to know the full 'unfired' molecular formula as long as when we are adding raw ball clay to a glaze recipe, we use the raw molecular weight.

So we can now add to our list of raw materials that we use in calculating out glaze recipes:

"Ball Clay QA... Formula (See bottom of the previous page.)
Molecular Weight: 369.8 (raw)
338.7 (calcined)"

The formula is fairly unwieldy, and in many cases it will be possible to simplify it. For example, if you just want to add 5% of ball clay QA to a glaze (to aid suspension, perhaps), you could fairly safely take the formula to be:

1.0 Al_2O_3. 3.59 SiO_2, with the molecular weights as above.

You would be ignoring the fluxes, iron and titanium. If, however, you were making up a glaze with, say, 35% of ball clay QA (perhaps for raw dipping), then the fluxes, iron and titanium start to become a significant proportion of the overall glaze, and the full formula should be used.

FORMULA TO RECIPE - A MORE DIFFICULT EXAMPLE

This section is not essential to the course. It is included, however, particularly for those wishing to handle more complicated examples of seger formula conversions. You will find that it is much easier than it looks. Those of you who have done no algebra should still be able to follow the section on simultaneous equations. But if it bothers you too much, omit this section until you really need it for your own work.

I will now illustrate a more complicated conversion from formula to recipe, using the ball clay formula and molecular weight that we worked out in the previous calculation:

Ball Clay QA — Molecular Weight (raw) — 369.8

Total KNaO = 0.10	0.04 K_2O		
	0.06 Na_2O	1.0 Al_2O_3	3.59 SiO_2
	0.02 CaO	0.02 Fe_2O_3	0.07 TiO_2
	0.09 MgO		

For the sake of the exercise, we will also use a 'real' feldspar formula. (You *should* be able to get a reasonably accurate analysis of your feldspar from your supplier.) Let us assume we are using Broken Hill feldspar with the following formula (taken from McMeekin):

Broken Hill Feldspar — Molecular Weight — 554

Total KNaO = 0.971	0.677 K_2O		
	0.294 Na_2O	1.108 Al_2O_3	5.917 SiO_2
	0.005 MgO		0.001 TiO_2
	0.023 FeO		

The 'Required Glaze' that I have chosen is a formula given by McMeeking for a 'Kaki' Glaze:

0.30 KNaO		
0.42 CaO		
0.02 MgO	0.81 Al_2O_3	4.00 SiO_2
0.25 FeO		
0.01 MnO_2		

Firstly, a few comments:

1. We want to use the Broken Hill feldspar as our main source of KNaO, and the ball clay QA as our main source of Al_2O_3. You will find that this provides us with an unusual problem (though it nearly always occurs when using ball clay and feldspar together). If we fill in (on our conversion chart) the requirement of KNaO first, as usual, we will get the first line as follows (using theoretical feldspar for simplicity):

Material	M.P.	----------	KNaO	----------	Al_2O_3	SiO_2
Feldspar	0.3	----------	0.3	----------	0.3	1.8

So far, so good. But when we come to make up the rest of the Al_2O_3 from ball clay QA, we find that we overload the KNaO, because *the ball clay contains some KNaO.*

Similarly, if we try filling the Al_2O_3 requirement first (with ball clay) we find when we come to top up the KNaO requirement, that we overload the Al_2O_3 because feldspar contains some Al_2O_3.

In this case, there is one mixture (and only one) of feldspar and ball clay that gives exactly the KNaO, and Al_2O_3 that we need, without overloading or underfilling either. To find this mixture, we can use trial and error or a simple algebra technique called simultaneous equations (see later).

2. Note the inclusion of MnO_2 (manganese dioxide) in the fluxes column. Although a colouring oxide, MnO_2 behaves as a member of the RO group, being a relatively active flux. At 535°C, MnO_2 breaks down to produce MnO (which now looks like a typical RO flux). The amount here is negligible but serves to illustrate the point.
3. Note also the inclusion of FeO (iron oxide) in the fluxes (RO) column. Under reduction, iron oxide in a glaze is largely 'reduced' to the ferrous form (FeO), and in this form, it acts as an RO flux. Under oxidation, much of the iron oxide exists in the glaze in the ferric form (Fe_2O_3), and as such could probably be excluded from the RO column and put into the R_2O_3 column. (Fe_2O_3 does still have a little fluxing power, according to Parmelee.) Assuming that we are firing under reduction, we will include the iron oxide in the fluxes. Actually, it does not matter to the recipe where you put it.
4. Materials used – apart from the chosen ball clay and feldspar – we will use whiting, magnesium carbonate (if necessary), black iron oxide, and silica, and we will assume that all ingredients except the ball clay and feldspar are pure enough to use the theoretical formulae and molecular weights.

Trial and Error

Getting back to point 1 in the comments above, if you do try to continue the calculation in the usual way, calculating to fill the alumina requirement with ball clay, the second line in the conversion chart would read:

Material	M.P.	----------	KNaO	----------	Al_2O_3	SiO_2
Ball Clay QA	0.51	----------	0.051	----------	0.51	1.83

By adding this to the feldspar figures in 1, you will see that the alumina requirement is filled (because we calculated it to be so) but the KNaO is already overloaded by 0.051 M.P. Therefore, you could try eliminating this overload by reducing the feldspar by 0.051 M.P. However, this will lead to a shortage of alumina. If you decide to make up for this by adding more ball clay, this will again cause an overload in KNaO but much smaller this time. You may decide that the discrepancy is now negligible or continue the process until it is.

Simultaneous Equations

We calculate the molecular parts of feldspar and ball clay simultaneously, using simple algebra as follows:

We want to know the M.P. of feldspar in the glaze.
Call this figure 'A' M.P.
We want to know the M.P. of ball clay in the glaze.
Call this figure 'B' M.P.
The sources of alumina for the glaze are the feldspar and the ball clay. Therefore:

Total A_2O_3 in glaze = Al_2O_3 from feldspar + Al_2O_3 from ball clay
= (M.P. feldspar x 1.108) + (M.P. ball clay x 1.0)

as per feldspar and ball clay formulae

= (A x 1.108) + (B x 1.0)
= 1.108 A + 1.0 B

However, we know that in the required glaze, the total alumina equals 0.81. Therefore, for the required glaze we can say that:

$$1.108\ A + 1.0\ B = 0.81$$ Let us call this equation (1).

The sources of KNaO in the glaze are, once again, the feldspar and the ball clay. Therefore:

Total KNaO in glaze = KNaO from feldspar + KNaO from ball clay
= (M.P. feldspar x 0.971) + (M.P. ball clay x 0.10)
= (A x 0.971) + (B x 0.10)
= 0.971A + 0.10B

However, we know that in the required glaze, the total KNaO equals 0.3. Therefore, for the required glaze we can say that:

$$0.971\ A + 0.10\ B = 0.3$$ Let us call this equation (2).

Write equations (1) and (2) out together as follows:

$$1.108\ A + 1.0\ B = 0.81 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$
$$0.971\ A + 0.1\ B = 0.3. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

We have two unknowns, A and B. In order to solve the equations, we must first eliminate one or other of these unknowns. This is done as follows:

Bring either A or B to unity in both equations. Since B is already at unity in equation (1), let us use B. Equation (1) therefore stays as it is. Equation (2) is divided throughout by the number that will bring 0.1B to unity (1.0B). To get any number to unity, you divide it by itself. Therefore, divide equation (2) by 0.1 to give the following:

$$9.71\ A + 1.0\ B = 3.0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Because everything is still in the same proportion, we can still call it equation (2).

Now set out the two equations again, using the new equation (2), and putting the one with the bigger numbers on top:

$$9.710\ A + 1.0\ B = 3.00 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$
$$\underline{1.108\ A + 1.0\ B = 0.81} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$
$$8.602\ A + 0.0\ B = 2.19 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

To get equation (3), I simply subtract equation (1) from equation (2). Thus we have got rid of B -- equation (3) can be rewritten:

$$8.602A = 2.19 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Therefore:
$$A = \frac{2.19}{8.602}$$
$$A = 0.255$$

Having found the value of A, we can substitute in either (1) or (2) to find B. Let us use (1):

$$1.108A + 1.0B = 0.81 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$
$$(1.108 \times 0.255) + 1.0B = 0.81$$
$$0.283 + 1.0B = 0.81$$

Therefore:
$$1.0\ B = 0.81 - 0.283$$
$$= 0.527$$
$$B = 0.527$$

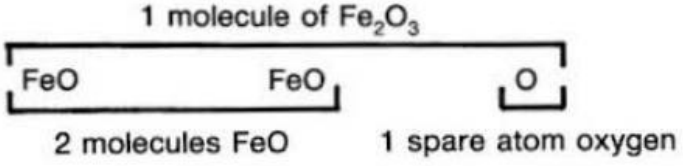
The proof of our mathematical pudding comes when we use these two numbers in the conversion chart, A for M.P. feldspar and B for M.P. ball clay. If our calculations are correct, this combination will give us the required amounts of KNaO and Al_2O_3.

Now work through the figures in conversion chart No.5 to make sure you follow. The calculations for line 1 and line 2 are shown on the bottom of the conversion chart.

*The molecular formula for ball clay QA indicated iron present in the Fe_2O_3 form, the amount being 0.02 M.P.

The required glaze formula calls for 0.25 M.P. of FeO, so we must convert this 0.02 M.P. of Fe_2O_3 into its equivalent in FeO.

To do this, rewrite the formula of Fe_2O_3 thus:



From this, we can see that:

1 molecule Fe_2O_3 gives 2 molecules FeO

Therefore: 0.02 M.P. Fe_2O_3 gives 0.04 M.P. FeO.

CONVERSION CHART 5:

					0.30 KNaO	0.42 CaO	0.02 MgO	0.25 FeO	0.01 MnO_2	0.81 Al_2O_3	4.00 SiO_2	0.0 TiO_2
Line 1	Broken Hill Feldspar	0.255	554.0		0.25		Negligible	Negligible		0.28	1.51	Negligible
Line 2	Ball Clay Q.A.	0.527	369.8		0.05	0.01	0.05	0.02		0.53	1.89	0.04
Line 3	Whiting	0.41	100.1			0.41						
Line 4	Silica	0.60	60.1								0.60	
Line 5	Manganese Dioxide	0.01	86.9						0.01			
Line 6	Black Iron Oxide	0.23	71.9					0.23				
TOTALS				TOTALS	0.30	0.42	0.05	0.25	0.01	0.81	4.00	0.04
NOTES:							Slight o' load					Not required
WORK OUT LINE 1 AS FOLLOWS:												
Broken Hill Feldspar 1 Molecule:		Multiply these figs:			0.971		0.005	0.023		1.108	5.917	0.001
		x 0.255 to										
0.255 M.P.:		get these:			0.247605		.001275	0.005865		0.28254	1.508835	0.000255
WORK OUT LINE 2 AS FOLLOWS:												
Ball Clay Q.A.	1 Molecule:	Multiply these figs:			0.1	0.02	0.09	0.04*		1.0	3.59	0.07
		x 0.527 to										
	0.527 M.P.:	get these:			0.0527	0.01054	0.04743	0.02108		0.527	1.89193	0.03689

* See pages 105 and 107 for comments on FeO and Fe_2O_3.

Also, while on the subject of iron oxide:

If you want to use red iron oxide (Fe_2O_3) instead of black (FeO), then Line 6 will be as follows:

Material	M.P.	M.Wt
Line 6: Red Iron Oxide	0.115	159.7 etc.....

THE PERCENTAGE METHOD OF GLAZE CALCULATION

A major disadvantage of expressing glazes as a molecular formula and working the recipe out from that formula is that analyses of raw materials (feldspar, ball clay etc.) provided by the rock miller are almost invariably expressed as a percentage analysis of the oxides present (% by weight). In order to use your ball clay, feldspar etc. in your calculations accurately, you must, therefore, first work out the molecular formula and molecular weight of the raw material. This is all right if you use only a few such materials -- an hour's calculation and you have all your % analyses converted to molecular terms. But if you work with a wide range of materials, it may be too much of a bother to convert all of them unless you have access to a computer. However, if your required glaze is expressed as a % analysis, and if you have the % analyses of all your raw materials, you can convert directly from % analysis to recipe using the Percentage Method. This method is clearly outlined in *Oriental Glazes* by Nigel Wood.

You may well ask, why then do we persist in using the Molecular Formula Method? If we are just interested in converting from an analysis to a recipe or back again, obviously we do not need to touch molecular theory. However, one of the main reasons for this book is to help readers come to grips with principles of glaze technology, to enable them to predict effects, to extrapolate and interpolate results, and, in general, to search in a systematic way for desirable results. These principles of glaze technology make more sense if the glazes are expressed as molecular formulae rather than as percentages because many of the oxides have similar properties and can be substituted for each other on a molecule for molecule basis without greatly affecting the result. For example, you can juggle around the alkali fluxes (R_2O group) taking out, say, 0.2 M.P. K_2O and replacing it with 0.2 M.P. Li_2O, and with the possible exception of glaze fit, the difference will usually be minimal. But if you take out, say, 5% by weight of K_2O and replace it with 5% by weight of Li_2O, the effect will probably be quite marked because in molecular terms you would be putting back three times more alkali flux than you removed. (Li_2O has a molecular weight less than one third that of K_2O.)

It seems to me that the Results Charts, expressed in molecular parts, tend to bear this out. Although we are making fairly major alterations to the fluxes from one set to another, and varying the alumina and silica over a very wide range, the overall patterns remain remarkably similar. Perhaps someone could come up with a similar system based on the percentage method, but I doubt it would have the same consistency.

Also you will find that much of the literature on glazes uses formulae expressed in molecular parts, so my own feeling is that anyone seriously into the theory of glazes (and not all serious potters are!) will benefit from being able to use both systems. I myself use the Percentage Method when it is convenient, but to 'understand' a glaze, I prefer to see it in molecular terms. I commend the Percentage Method as a useful skill and recommend Nigel Wood's book as an excellent introduction to oriental glazes and the Percentage Method. It also contains a section on Simultaneous Equations.

MORE FORMULA TO RECIPE

Here are two more formula-to-recipe conversions to illustrate some points that beginners sometimes find difficult, the first involving talc, and the second using a commercial frit as ingredients.

EXAMPLE A

Calculating the recipe of a high alumina magnesia glaze (Glaze A) using talc as the source of MgO, and a combination of kaolin and alumina hydrate to top up the requirement of alumina. See Conversion Chart No.6:

CONVERSION CHART 6:

					REQUIRED GLAZE				
				Glaze A	0.2	0.4	0.4	0.8	2.5
Line	Raw Material	M.P.	M.Wt	etc. . . .	KNaO	CaO	MgO	Al_2O_3	SiO_2
1	K-Feldspar	0.2	556		0.2			0.2	1.20
2	Talc	0.13	379				0.39		0.52
3	Kaolin	0.39	258					0.39	0.78
4	Alumina Hydrate	0.21	156					0.21	
5	Whiting	0.4	100			0.4			
			Oxide Totals:		0.2	0.4	0.39	0.80	2.50

If you can already 'read' the workings of this chart, enough said; if not, read on.

Order of Calculation

The normal order of calculation is changed in this case because the glaze is very low in silica; we want to use talc and as much kaolin as possible; and both of these add silica to the glaze and could overload it. In this case, the order will be:

KNaO, MgO, SiO_2, Al_2O_3, CaO.

It is not possible for me to give any firm rule on order of calculation, except to say that you should always start with that recommended in the first example given in this chapter, and if overloading occurs, a new order will immediately suggest itself to you.

Comments on the Conversion Chart

If you need to, you can still work through each line using the four question technique. However, I will explain it here in a more abbreviated style:

Fill in the amounts of oxides for Glaze A under 'Required Glaze' (see Conversion Chart No.6).

Line 1

Now fill the requirement for KNaO (or call it K_2O if you prefer) using K-feldspar. The required 0.2 M.P. of KNaO will be provided by 0.2 M.P. of feldspar, and this amount of feldspar will also introduce 0.2 M.P. of Al_2O_3 and 1.2 M.P. of SiO_2 into the glaze. Insert these four figures in Line 1.

Line 2

Next comes MgO. Using talc will raise two problems. The first of these is calculating the number of M.P. of talc that will give us the required 0.4 M.P. of MgO. This is done as follows:

Consider the formula for talc:

one molecule of talc

3 MgO.	4 SiO_2	H_2O
3 molecules of MgO	4 molecules of SiO_2	1 molecule of water

Thus we can see that 1 molecule of talc will provide 3 molecules of MgO, and we can set the problem out as follows:

1 M.P. of talc gives 3 M.P. of MgO (ratio of 1:3)

x M.P. of talc gives 0.4 M.P. of MgO.

To maintain the 1:3 ratio, x must be one third of 0.4.

Therefore $x = \frac{0.4}{3} = 0.13333$ M.P. talc.

The 0.13 M.P. talc will provide 0.39 M.P. MgO, and 0.52 M.P. SiO_2 (i.e. 0.13 x 4). (Usually there is no point in using more than two decimal places.)

Insert these three figures in Line 2.

Line 3

Now for silica. We come here to the second problem arising from our use of talc for Glaze A. If we were to fill the requirement for Al_2O_3 before SiO_2 (as we usually do) using all kaolin, we would immediately have too much silica (1.2 M.P. from feldspar, plus 0.52 M.P. from talc, plus 1.2 from the amount of kaolin that would be necessary, equals a total of 2.92 M.P. of silica, which is too much). So what we do is to fill the requirement of SiO_2 first, *using kaolin as the source of silica*, thus:

We already have 1.72 M.P. SiO_2 from the feldspar and talc. Therefore we need 2.5 − 1.72 = *0.78*M.P. SiO_2 to be provided by kaolin.

1 M.P. kaolin provides 2 M.P. SiO_2 (see the formula for kaolin).

x M.P. kaolin provides 0.78 M.P. SiO_2.

To maintain the 1:2 ratio between kaolin and silica, it is obvious that x will have to be half of 0.78.

Therefore x = 0.39

So we use 0.39 M.P. kaolin to provide the required 0.78 M.P. of silica, and this will also bring into the glaze 0.39 M.P. Al_2O_3...

Insert these three figures in Line 3.

Line 4

We now top up the alumina, but using either 'alumina' (Al_2O_3, M.Wt. 102) or preferably 'alumina hydrate' ($Al_2O_3.3H_2O$, M.Wt.156). Theoretically we could have used alumina without using kaolin to provide the alumina requirement, thereby avoiding the possibility of overloading the silica, but we want as much kaolin as possible for ease of suspension of the glazes (The kaolin being a clay is our main suspending agent), and also because pure alumina tends to promote matts more than alumina that is introduced in the form of clay or feldspar, probably because of incomplete incorporation of the pure alumina, especially in a quick firing. Let us use alumina hydrate since it does have some effect in aiding glaze suspension. (Make sure it is 300 mesh or finer; some alumina being presently sold is relatively coarse, and even 200 mesh will not fully incorporate into the glaze if the firing is not reasonably soaked at maturity.)

We require a total of 0.8 M.P. alumina in the glaze. We already have 0.59 M.P. from feldspar and kaolin. We need a further 0.21 M.P. from alumina hydrate.

From its formula, we can see that one molecule of alumina hydrate will provide one molecule of Al_2O_3.

Therefore, our 0.21 M.P. Al_2O_3 will be provided by 0.21 M.P. of alumina hydrate.

Enter these two figures in Line 4.

Line 5

In the same way as we did for limestone glazes, we will use 0.4 M.P. whiting to provide the 0.4 M.P. of required CaO.

Enter these two figures in Line 5.

Add up the oxide totals to check that they are correct.

EXAMPLE B

Calculating the recipe of a high soda glaze (Glaze B) using a frit as the source of soda: The required glaze is listed in the conversion chart, and the frit we are going to use is Podmore's Frit P.2250, which has the formula 0.8 KNaO, 0.2 CaO, 0.1 Al_2O_3, 1.5 SiO_2, 0.1 B_2O_3. (Molecular Weight = 176.)

CONVERSION CHART 7:

Material	Molec. Parts	Molec. Weight	Parts by Weight	%	REQUIRED GLAZE KNaO 0.8	CaO 0.2	Al_2O_3 0.8	SiO_2 2.5	B_2O_3 0.1
Frit P.2250	1.0	176	176	52.3	0.8	0.2	0.1	1.5	0.1
Kaolin	0.5	258	129	38.4			0.5	1.0	
Alumina Hydrate	0.2	156	31.2	9.3			0.2		
		Totals:	336.2	100.0	0.8	0.2	0.8	2.5	0.1

Notes:

a. The boric oxide is unavoidable as it is incorporated into the frit.

b. In Glaze B, it is not possible to use kaolin alone in Line 2 of the conversion chart to top up the alumina to the total required. If this were done, we would overload on the silica by 0.4 M.P. Therefore we use kaolin to top up the *silica* requirement, and then use alumina, or alumina hydrate to top up the Al_2O_3 requirement.

c. If you have worked through the previous examples, you should be able to follow the workings of the conversion chart. If, however, you have trouble with the frit, think of it as having the molecular formula:

$$0.8\ KNaO,\ 0.2\ CaO,\ 0.1\ Al_2O_3,\ 1.5\ SiO_2,\ 0.1\ B_2O_3 \ldots\ldots !$$

which is somewhat more complicated than the molecular formula for feldspar but is handled in exactly the same way. You could use the Four Question Technique to get line 1 as follows:

Q1. How much KNaO do we need?
A. 0.8 M.P.

Q2. What material will we use to give this KNaO?
A. Frit P.2250.

Q3. How many M.P. of frit P.2250 will give 0.8 M.P. of KNaO?
A. 1.0 M.P. of frit.

Q4. What other materials, apart from the 0.8 KNaO, does this 1.0 M.P. of frit introduce into the glaze?
A. 0.2 CaO, 0.1 Al_2O_3, 1.5 SiO_2, 0.1 B_2O_3.

CALCINING CALCULATIONS

You will sometimes wish to substitute calcined clay for raw clay in a glaze recipe. The calcined equivalent of the raw material can be easily calculated using the following formula:

$$\text{calcined clay \%} = \text{raw clay \%} \times \frac{100 - \text{L.O.I.}}{100}$$

Where 'L.O.I.' is the percentage loss on ignition, usually available from an analysis sheet.

In the special case of pure kaolin, this formula works out to be:

$$\text{calcined kaolin \%} = \text{raw kaolin \%} \times 0.86 \text{ (approx.)}$$

PARTS CHART CALCULATIONS

Herewith one final detail of experimental technique with our biaxial blending, i.e. how do we arrive at the numbers in the 'Parts Chart'? If you want to compile an experiment with other than a 5 by 7 format, then you will need to work out your own 'Parts Chart'.

See Chapter 6, Diagram 6.1. The way you arrive at the numbers is as follows:

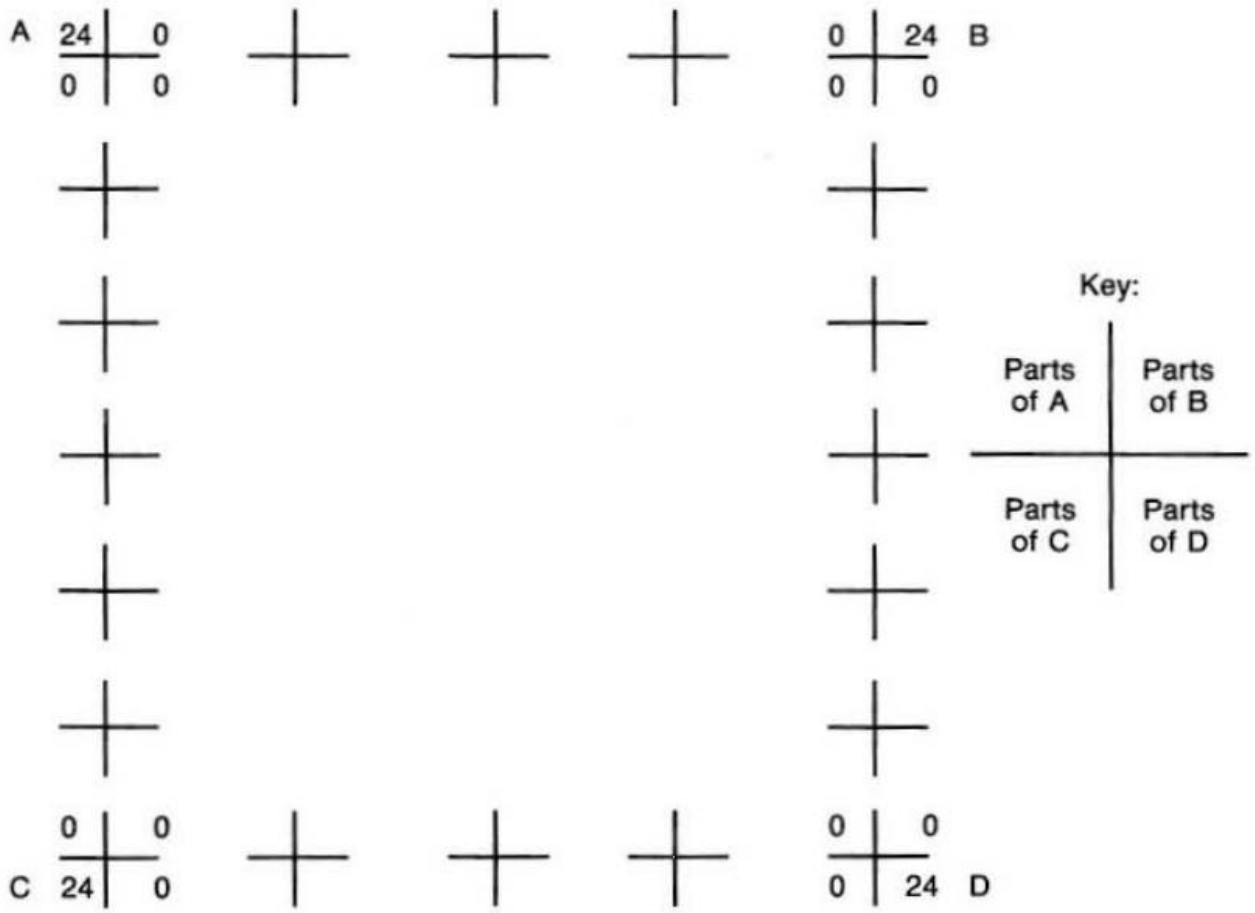
Our biaxial format contains 5 glazes by 7 glazes, and we calculate the 'most convenient parts total' thus:

$$\begin{aligned} \text{Format:} &= 5 \times 7 \\ \text{Most convenient parts total} &= (5 - 1) \times (7 - 1) \\ &= 4 \times 6 \\ &= 24 \end{aligned}$$

The 'most convenient parts total' is calculated such that the parts numbers in the Parts Chart are all whole numbers and as small as possible.

Note that the parts total used in the base glaze experiments is 96 parts, and that this is a simple multiple of 24. First, I will show you how to work out the Parts Chart for a parts total of 24. Having decided to use 24, put 24 parts of Glaze A, B, C, and D on the respective corners of the grid and fill in the zeros thus:

DIAGRAM 14.1



Now looking at the top line, going from glaze A to glaze B, the parts of glaze A used will go from 24 to zero in 4 steps (i.e. 5 − 1). That means that each step must be 6 parts less than the previous (24 ÷ 4 = 6) as you progress from A to B.

We can now draw in the top line for glaze A thus:

24	0		18			12			6			0	24
0	0											0	0

To get the top line for glaze B, you simply reverse the numbers so they descend from glaze B (24 parts) to glaze A (zero parts of B) thus:

	0			6			12			18			24

In the top line there is no glaze C or glaze D, so it is zeros all the way. So the top line now looks like this:

24	0		18	6		12	12		6	18		0	24
0	0		0	0		0	0		0	0		0	0

The bottom row from glaze C to glaze D is done in exactly the same way, to give:

0	0		0	0		0	0		0	0		0	0
24	0		18	6		12	12		6	18		0	24

Now you do the two vertical borders, A-C and B-D. In this case you go from 24 to zero in 6 steps (i.e. 7-1). That means that each step must be 4 parts less than the previous (24 ÷ 6 = 4). We can now draw the A-C border as follows for glaze A:

24	

20	

16	

12	

8	

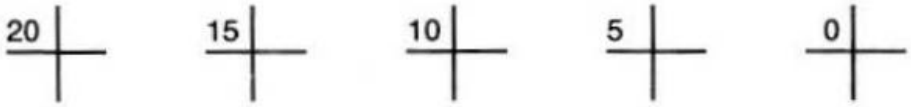
4	

0	

Reverse these numbers for glaze C. Glazes B and D will be all zeros along this border. And similarly you work out the B-D border.

You now have the parts numbers for all the glazes around the borders, and you can work across or down to fill in the inside glazes.

For example, on the second row (glazes 6 to 10), glaze A will go from 20 parts to zero in 4 steps, i.e.:



And so you keep filling it all in until you have the complete Parts Chart as follows:

DIAGRAM 14.2

24 | 0 0 | 0	18 | 6 0 | 0	12 | 12 0 | 0	6 | 18 0 | 0	0 | 24 0 | 0
20 | 0 4 | 0	15 | 5 3 | 1	10 | 10 2 | 2	5 | 15 1 | 3	0 | 20 0 | 4
16 | 0 8 | 0	12 | 4 6 | 2	8 | 8 4 | 4	4 | 12 2 | 6	0 | 16 0 | 8
12 | 0 12 | 0	9 | 3 9 | 3	6 | 6 6 | 6	3 | 9 3 | 9	0 | 12 0 | 12
8 | 0 16 | 0	6 | 2 12 | 4	4 | 4 8 | 8	2 | 6 4 | 12	0 | 8 0 | 16
4 | 0 20 | 0	3 | 1 15 | 5	2 | 2 10 | 10	1 | 3 5 | 15	0 | 4 0 | 20
0 | 0 24 | 0	0 | 0 18 | 6	0 | 0 12 | 12	0 | 0 6 | 18	0 | 0 0 | 24

Notes:

1. Check your arithmetic by adding the four numbers for each glaze. They should total, in this case, 24.
2. To get the Parts Chart used in the base glaze experiments, multiply all the numbers in Diagram 14.2 by 4. The reason I chose 96 was that I wanted approximately 100 mL of each glaze to provide enough for a small group of people.

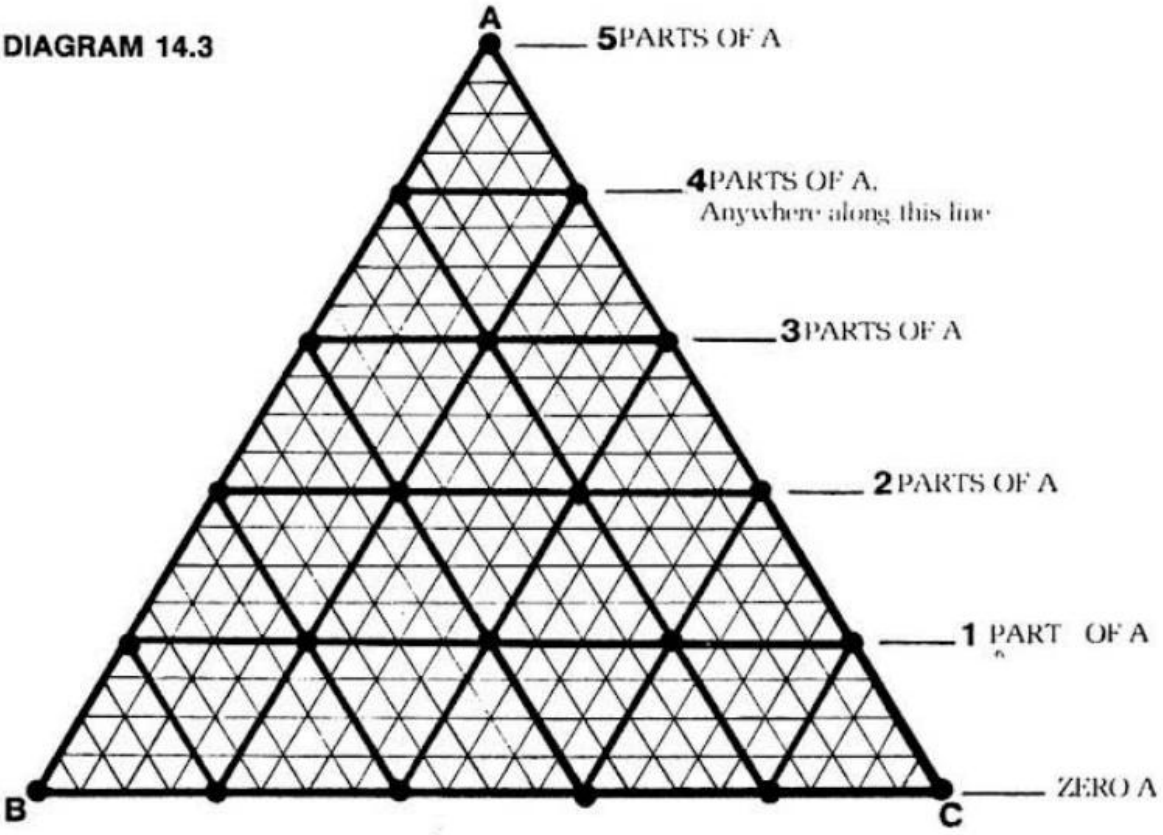
'Parts Chart' for a Triaxial Diagram

This is rather simpler to do than the previous example. See Diagram 14.3. If you want 6 glazes along each side of the triangle (i.e. 21 glazes over the whole diagram), then you firstly get the parts for glaze A as follows:

Draw the lines parallel to B-C as shown so that they intersect the intermediate glaze points on A-B and A-C.

All the glazes on line B-C will have zero parts of A.
On the next line above, all the glazes will have 1 part of A.
On the next line, all the glazes will have 2 parts of A.
And so on, until you reach the apex of the triangle, which represents glaze A.
Then you turn the diagram around and do it for B, and then for C.
When you add up the total of parts of A, B and C for each of the 21 glazes, they will each total 5 parts.

DIAGRAM 14.3



PARTIAL BLENDS AND INTERMEDIATE BLENDS

You may find you wish to examine a small area of one of the 5x7, 35 glaze grids presented here without having to make up all 35 glazes. If you do this the right way, you will get exactly the same glazes produced by the larger grid, so that *all of the data on recipes, formulae and oxide wt % etc. given in the Data Sheets still apply.*

Suppose that AB, CD represents the 35 glaze grid and WX, YZ represents the area you wish to study (see Diagram 14.4). Obtain the recipes for W, X, Y and Z (glazes 11, 13, 26 and 28) from the appropriate Data Sheet. These are the 'corner glazes' for the partial blend. Work out a Parts Chart for 3 glazes across by 4 down (see previous section). The resultant 12 glazes will be as shown on the diagram within the bounds of WX, YZ, and the recipes etc. can be read off the original Data Sheet.

DIAGRAM 14.4

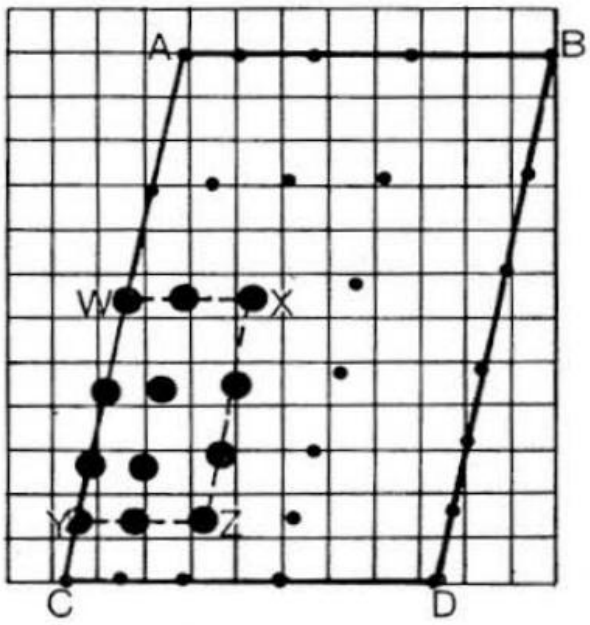
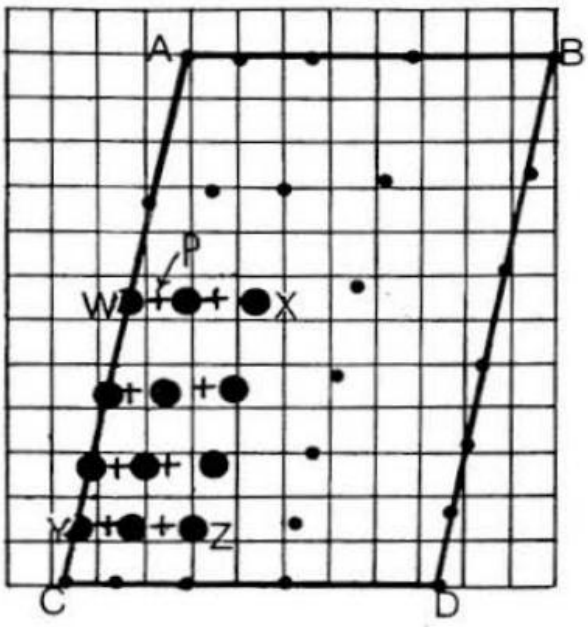


DIAGRAM 14.5



You may decide that the intervals are too far apart for your purposes. This will sometimes happen in isolated areas on a 35 glaze grid. For example, you may decide the jumps in silica are too large. If you look again at the partial blend WX, YZ, you can easily insert two intermediate lines as indicated by the crosses (+). See Diagram 14.5. In this case, you would use a Parts Chart for 5 glazes across by 4 down. All the original data still applies for the original 12 glazes. The recipes and oxide weight % figures for the intermediate (+) glazes can be easily calculated since they are midway between the values given for the two adjacent glazes. For example, the recipe for Glaze P is exactly midway between the recipes given on the Data Sheet for Glazes 11 and 12. (This applies also to the oxide weight % figures, but not exactly for the Seger Formula; however, on this scale the difference is so small as to be negligible.) The simplest arithmetical technique for getting the recipe of Glaze P is to add the two recipes together (11 and 12) ingredient by ingredient. Divide throughout by 2 if you wish to get back to percentage figures.

CALCULATING BLENDED GLAZE RECIPES

These calculation techniques are necessary only if designing your own experiments such as was suggested for Experiment 10. The recipes for all the 8 main sets and the intermediate sets are given in the Data Sheets.

Method 1 - Parts Chart Method

Note: The 'Corner Glazes' mentioned in these examples were used as the limits of the Limestone Set in the original AFAS course. They are not used in any of the current sets, but as examples of the technique, they are still quite valid.

You can use the 'Parts Chart' and a calculator to work out the nett recipe for any intermediate glaze. For example, if we want Glaze No.29, we can get the proportions of Glazes A, B, C and D from the Parts Chart Thus:

Glaze 29 consists of... 4 parts of Glaze A
12 parts of Glaze B
20 parts of Glaze C
60 parts of Glaze D

If we now take the four corner glaze recipes one at a time and multiply the recipe for A by 4, for B by 12, C by 20 and D by 60, and then add up the 4 figures for feldspar, the 4 for whiting, the 4 for kaolin and the 4 for silica, these totals, represent a recipe for glaze No.29. There will be 9600 parts in the total; so if you want your recipe expressed as percentages, you will have to divide each ingredient by 96. The figure of 96 is a result of having a total of 96 parts in each of the glazes on the Parts Chart. See Diagram 14.6.

DIAGRAM 14.6

	FELDSPAR	WHITING	KAOLIN	SILICA
GLAZE A x 4	31.6 x 4 = 126.4	22.7 x 4 = 90.8	44.0 x 4 = 176.0	1.7 x 4 = 6.8
GLAZE B x 12	18.8 x 12 = 225.6	13.5 x 12 = 162.0	26.1 x 12 = 313.2	41.6 x 12 = 499.2
GLAZE C x 20	41.3 x 20 = 826.0	29.7 x 20 = 594.0	0	29.0 x 20 = 580.0
GLAZE D x 60	21.8 x 60 = 1308.0	15.7 x 60 = 942.0	0	62.5 x 60 = 3750.0
Parts (Total: 9600):	2486.0	1788.8	489.2	4836.0
Percentage (Total: 100):	25.9%	18.6%	5.1%	50.4%

Note: The total parts in the second last line may vary slightly from 9600 if any of the four original recipes did not contain exactly 100.0 percentage parts.

Method 2 - Graphical Method

This method will only work for line blends, but has some particular advantages, and it is a good visual illustration of the nature of line blends, so it is given here.

We use a sheet of graph paper (see Diagram 14.7). We want to discover the recipe of glaze No.21. This glaze is on the line blend between glaze A and glaze C, and we know the recipes of both these glazes. Draw a horizontal line on the graph paper representing the line blend. Mark off 7 equal divisions, representing the 7 glazes in the line blend A...C, and at A and C, draw vertical lines for the percentages as shown.

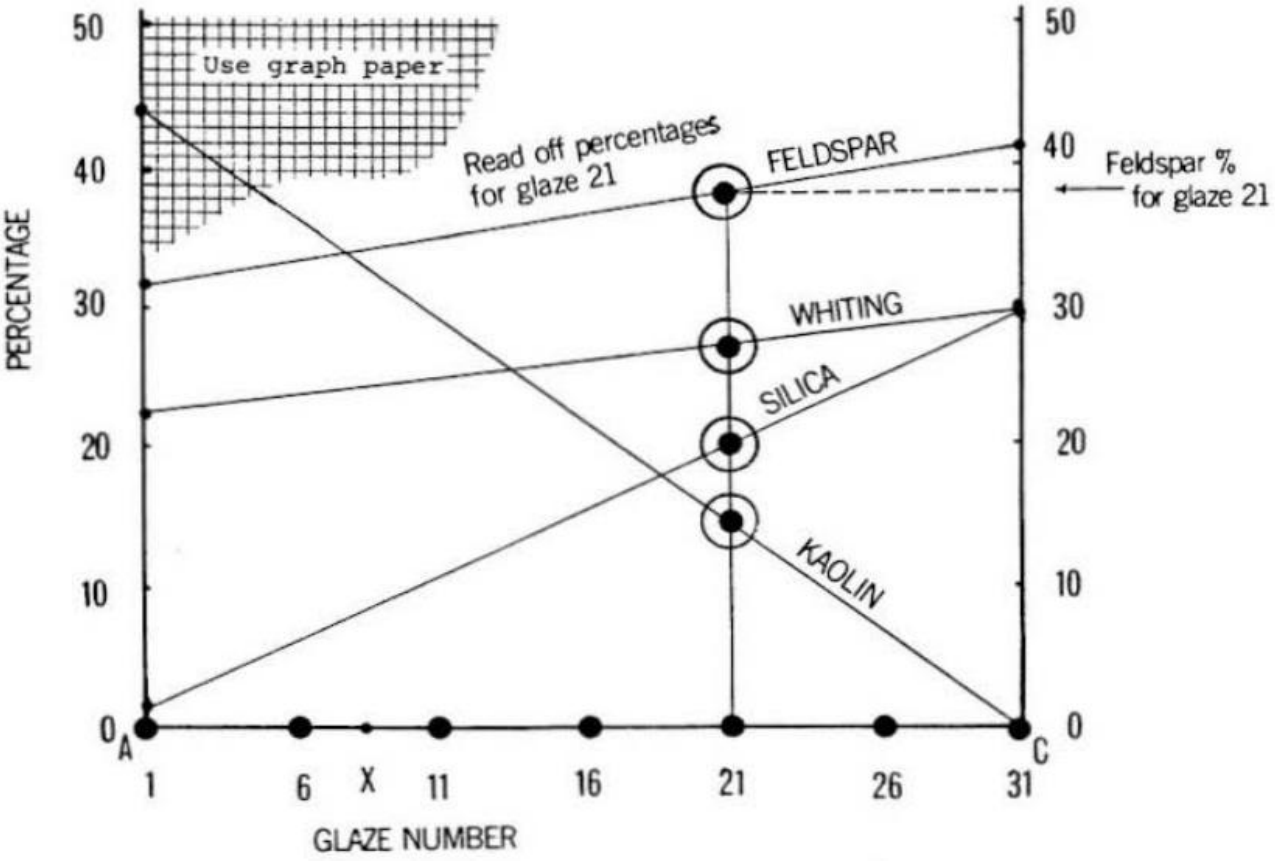
The recipes of corner glazes A and C are as follows:

	Glaze A	Glaze C
Feldspar	31.6	41.3
Whiting	22.7	29.7
Kaolin	44.0	0
Silica	1.7	29.0

Plot the materials on the graph paper one at a time as follows — we will do feldspar first:

On the vertical line above glaze A, plot a point at 31.6%.
On the vertical line above glaze C, plot a point at 41.3.%

DIAGRAM 14.7. Graph to calculate the Recipe of any Glaze in the Line Blend between Glaze A and Glaze C.



Now draw a *straight* line between these two points. You can now read off the feldspar percentages for *any* glaze on the line blend A...C, by seeing where that glaze intersects the feldspar line. For example, glaze No.21 will have approximately 38% feldspar (see dotted line). The other three raw materials are handled the same — you can read off the percentages for glaze 21 from the intersection points circled on the diagram. Thus, the recipe for glaze 21 (to the nearest %) is:

Feldspar	38
Whiting	27
Kaolin	15
Silica	20

Check to see they add up to approximately 100%. To get the figures more accurate than this, you would have to use a larger piece of graph paper.

It is possible to use this technique for glazes occurring inside the four bordering line blends. For example, we have already got the recipe for glaze 21. We could draw another graph for the line blend B . . . D, and get the recipe for glaze 25. We could now draw a third graph to give us the line blend from 21 to 25, and obviously we could read off from it any glaze belonging to that line blend. So one could theoretically use this cumbersome technique to obtain any glaze in the set by doing three graphs.

One of the advantages of the Graphical Method is that it is easy to work out recipes for intermediate glazes, e.g. if you want a glaze halfway between the adjacent glazes 6 and 11, it is just a matter of drawing a line up from the point X on Diagram 14.7 and reading the percentages.

PART II

SPECIFIC GLAZES

15 METHODOLOGY

In seeking to discover or reproduce glazes of any type, you soon learn that there are vital considerations other than the glaze recipe. The clay body on which it is fired and the kiln and firing cycle all have an effect, and with some glazes, the latter factors are decisive in achieving a certain result.

Although most of our systematic work relates to the glaze recipe, I will also frequently stress the need for varying body and firing conditions. The following are important factors that must be considered with most glazes:

Glaze Recipe:
- Molecular formula
- Alumina/silica ratio
- Details of the raw materials used
- Special preparation (e.g. ball milling) or application techniques

Clay Body or Slip Under the Glaze:
- Presence of iron or titanium oxides
- Whether porous or vitreous when fired
- Whether highly siliceous, or highly aluminous
- Body texture — mesh size, presence of grog, sand, iron spots etc.

Firing Conditions:
- Time temperature considerations during maturing of the glaze
- Time temperature considerations during the cooling cycle
- Kiln atmosphere
- Kiln type, fuel type etc.

With each glaze type that I discuss, I will list the factors that are important.

Those of you who have completed the section on base glazes will find that many glaze phenomena are explainable by the systematic work you have already done, varying fluxes, alumina, silica and firing conditions. Also the colouring oxide applications should give some indication of their behaviour when mixed into different base glazes.

A REFERENCE FRAMEWORK FOR MOLECULAR FORMULAE

When one considers glaze molecular formulae, there is an enormous range of possible values of fluxes, alumina and silica, and it is hard to know where to start. One way of teaching glaze theory in Japan involves relating the molecular formula of a particular glaze back to a 'standard' such as:

Standard Cone 10 Limestone Glaze:

$$\begin{matrix} 0.3\ K_2O \\ 0.7\ CaO \end{matrix}\ 0.5\ Al_2O_3\ 4.0\ SiO_2$$

It is important to have at least one standard fixed in your mind as a reference point. The reason this particular limestone glaze is so useful as a standard is that it lies right in the middle of the transparent shiny glaze zone (if you can imagine an alumina/silica chart for limestone glazes at cone 10) — and from this central standpoint, if you alter alumina, or silica or the fluxes, the effects will be fairly predictable within reasonable limits. However, if you have conscientiously completed the section on Base Glazes, you will now have not just one glaze, but an extensive reference framework to which you can relate the vast majority of glazes. And because you have done this basic research in a systematic fashion, you will be able to see cause and effect, see which variables are important and which not, and in general, predict and interpret glaze behaviour more confidently. I will be making repeated reference to the base glaze sets in the work that follows, using them as a starting point from which to develop an in-depth understanding of each particular glaze. Furthermore, the reason that our main study of natural glazes is left to the end of the course is that by then you will have a much deeper understanding from the systematic work done earlier, enabling

you to more accurately guess the contents of a natural ingredient such as ash or rock by observing its behaviour in a glaze.

TEST FIRINGS

There comes a point where you are reasonably sure your glaze recipe and clay body are correct, and more effort is needed to be put into the firing. If you had a test kiln, such as described in Chapter 15 of Tichane (see References), testing the important firing factors in any glaze would be easy. However, most of us make do with the kiln we have in the best way we can. (This has an advantage: sometimes a glaze evolved in a test kiln will not translate easily, if at all, to the production kiln, because of unmeasurable firing parameters.) Here are a few ways of getting a wide range of firing conditions with the kiln(s) at your disposal:

1. Obviously you could do a series of firings varying temperature, time and atmosphere factors, but this will probably be impractical in a large kiln.

2. Even if you do your normal firing, there is a greater range of conditions existing in the firing than you normally use, e.g. very high temperature (and usually stronger reduction) right in front of a gas burner, or on top of a bag wall; low temperature near the flue, or inside the flue outlet, or in the space under the bottom kiln shelf that is normally not used in some kilns; plus the normal variation that you experience throughout the setting.

3. You might encourage a very uneven firing to get a greater range of effects, e.g. if the kiln uses two burners, try to fire it on one . . . or leave out the bag wall . . . or pack cold spots densely with pots to make them even colder, while leaving the hot spots vacant, except for test pieces.

4. If you have a fibre kiln up to, say, 6 or 8 cubic feet, bear in mind that it costs very little to fire it empty, with just a few tests scattered. So even though a lot of space may be 'wasted', you can use it as though it were a much smaller 'test-kiln'.
5. Put tests in a friend's kiln, especially if the kiln or firing cycle is substantially different from your own.
6. Use draw trials as the glaze matures, numbering each draw trial after it is removed, and noting this on the kiln log. If crystal growth is important, you could take out draw trials as the kiln cools. Leave one draw trial in the kiln and compare this with one taken out just before turning off the kiln. Any difference between the two will be due to factors in the cooling cycle and should suggest desirable ways of altering this part of the firing. If you need to, you can put several different glazes on one draw trial (see below).

Having decided how you are going to vary the firing conditions, make multiple copies of the *few* glaze recipes (and body types) you are going to try, spread them around the kiln, and fire.

If you obtain a desired result in some odd part of your kiln or your friend's kiln, you then have to sit down and figure out what it is that is special about that part of the kiln so you can try to obtain the same conditions throughout your firing.

DRAW TRIALS

The oldest method of accurately determining glaze maturity involves removing glazed samples from the kiln during the maturing stage of the firing. Although it is not as convenient as observing pyrometric cones, it is still the best way to decide when to stop firing because you are observing first hand the conditions of clay and glaze inside the kiln. (This assumes you are using the same materials in the draw trial as in the pots.)

Draw trials may also be used to gain a better understanding of a glaze, by drawing samples from the time it starts to melt until maturity and also in the cooling cycle.

It is also fairly common to use draw trials of an unglazed iron-bearing clay that fires grey in reduction and terracotta colour in oxidation to give an indication of kiln atmosphere, i.e. reducing or oxidising.

In some traditional potteries, the technique of removing a complete pot is still used; however, draw trials are usually a 'test-ring' of clay, well flattened on the base so it is very stable, which is removed with a poker through the spyhole. I often use a flat tile suspended on kiln wadding to enable me to get underneath with a flat iron poker for easy removal. This allows a number of glazes to be used on the one tile; sometimes I use assessment tiles, enabling 35 glazes to be drawn at once, or

even more if several tiles are stacked. For determining the end point of a firing, rings are better; if just the top half of the ring is glazed and the glaze applied thickly, a roll will form at the bottom line of glaze as it matures, giving a useful added clue to help you decide when to finish.

It should be understood, however, that with many glazes the appearance of the glaze on a draw trial may be quite different to a similar sample left to cool in the kiln, even if the firing is terminated immediately the draw trial is taken. This particularly applies to matt glazes where the mattness is due to crystals forming in the slow cooling in the kiln. However, a little firing experience will give one the knowledge needed to understand the relationship between what is on a draw trial and what will be on the pots after cooling.

The use of draw trials is an important technique; and for someone studying glazes and clays, the ability to remove samples during the firing is essential. Unfortunately, many commerially made kilns are still designed by combustion engineers rather than potters, and they seem to expect one to work through a keyhole. However, this is changing as we make our needs knows to the designers. A spyhole the size of the end of a brick is ideal, though a smaller size can be used. If your spyhole is too small, make it larger.

Some other useful references to read on the subject of draw trials (usually listed in the index under 'test rings') are:

1. *Pioneer Pottery* by Michael Cardew (Longman, Cheshire)

2. *Notes for Potters in Australia* by Ivan McMeekin (NSW University Press).

3. *A Potter's Book* by Bernard Leach (Faber and Faber).

4. *Handbook for Australian Potters* by DeBoos, Harrison and Smith (Methuen).

OXIDATION — NEUTRAL — REDUCTION ATMOSPHERES

The term *oxidation* means that there is excess oxygen in the kiln above what is required for most efficient combustion.

Reduction means that there is not enough oxygen entering the kiln for full combustion, and this oxygen deficit means that there is, in fact, excess carbon monoxide (CO) and hydrogen present that would burn if extra oxygen were provided. The carbon monoxide and hydrogen are 'hungry' for oxygen and take it out of glazes and clays, and anything else present that contains oxygen, and this is the process of 'reduction'.

The term *neutral* refers to that balance point between oxidation and reduction where there is no spare oxygen and also no carbon monoxide or hydrogen. It represents the most efficient combustion point, where maximum use is made of the fuel as a heat source. In oxidation, the excess air has a cooling effect, and in reduction, the excess fuel also has a cooling effect and fuel is being wasted. So obviously a means of measuring oxidation/reduction will benefit fuel economy, as well as indicate kiln atmosphere.

Carbon dioxide (CO_2) is present in all stages of combustion, and, in fact, it is usually carbon dioxide that is being measured in most oxidation/reduction meters that potters use.

Many people will not have access to this kind of tool, and I will just give a few hints on reducing a downdraft gas kiln. Of course, if you buy a kiln, you should be able to get instructions on how to do a reduction firing, but if for any reason you are having trouble getting reduction, the following is a guide to get you started. The technique is a little wasteful of fuel, but if you do not have a reduction meter, you can use this technique to get reduction working, and then cut back on fuel (firing by firing) as you gain experience, without losing reduction.

I usually start reducing around 1000°C and continue the reduction until about 1200°C at least, for a 1280°C firing. I do not use the damper but simply increase gas pressure by 50 — 100% and close off the air until I have about the same temperature rise as when I was oxidising (100 — 150°C per hour). A strong reduction will be indicated by flame around the spyhole (the flame usually goes into the kiln unless the damper is closed) and stronger reduction by flame lapping around inside the kiln chamber. Smoke coming from the chimney in an L.P. gas kiln indicates very strong reduction. Most reduction effects do not require this degree of reduction. If you want very strong reduction, but your kiln is slightly underpowered for the job, you will find it difficult to get it and a temperature rise at the same time. All you can do here is have periods of less strong reduction, or perhaps even oxidation, to get the temperature to rise.

If the kiln has enough chimney to actively suck the kiln gases out, some degree of negative pressure is developed in the chamber as long as this 'sucking' process continues. If this is the case, it is usual to use some damper during reduction to prevent oxidation around cracks, spyhole etc. where air is being sucked into the kiln. The damper is closed off until the flame protrudes from the spyhole, rather than burning back into the kiln. Alternatively, if the kiln can be properly sealed, this should not prove a problem.

Reference: R. C. Brodie, *The Energy-Efficient Potter*, Watson Guptil.

MORTAR AND PESTLE LINE BLENDING TECHNIQUE

Suppose you have a 'fixed' part, e.g. 100 grams of a base glaze, and a 'variable' part, e.g. increasing amounts of opacifier, say, 1%, 2%, 4% etc. to give us a range of glazes with a steady increase in the opacifier content.

You take the fixed part of the glaze, weighed out, made up with water, and put through a sieve, and dip in a couple of test pieces.

Note: You must take enough samples for what you require at this point because you will now change the glaze to get the second glaze — and then it will be too late to sample for the first. This procedure applies all the way through.

You then start adding the variable part, in this case an opacifier. Add, say, 1% of opacifier to glaze, grind it well in the mortar and pestle (and, if necessary, sieve it again) and take a second lot of samples.

Then add an extra 1% (total 2%) opacifier and repeat the process. A line blend can be done quite quickly this way, especially if sieving is not necessary after every addition. If the variable part is something like iron oxide (obviously not in this case), then it will probably mix in well, but opacifier additions may need sieving.

It is important that the volume of sample taken each time be negligible compared with the total volume of glaze being used, otherwise the actual percentages being added will be a lot more than indicated by the calculations. This technique, therefore, is better for individuals than large groups.

16 CRYSTALLINE GLAZES

The reason for treating crystalline glazes early in Part II is that crystal formation and growth is a widespread glaze phenomenon, and an understanding of crystals is necessary if one is to understand the behaviour of many glazes. Note that I will use the term *crystalline glaze* to refer to any glaze where the crystals are visible to the naked eye, but the principles discussed here apply equally well to crystals of microscopic size, which are responsible for many matt glazes, and also, it would seem, for some opalescent glazes (see Parmelee page 212), opaque glazes, and copper reds (see Parmelee pages 465-472) etc.

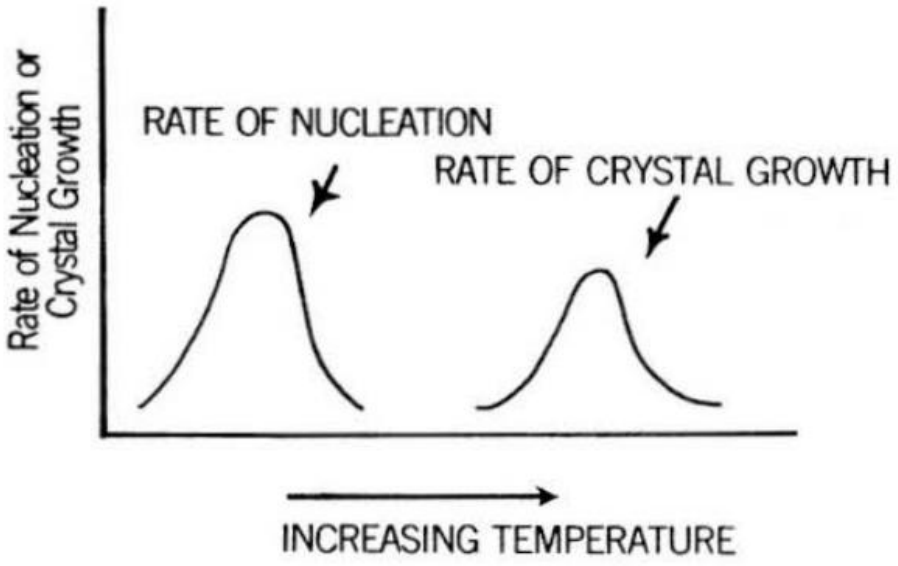
DEVITRIFICATION — GLASS GIVING RISE TO CRYSTALS

It is not my intention to cover glass and crystal theory in detail in this course, as this theory is very adequately covered elsewhere. For an introduction to the subject, read the suggested text, by Fraser, Chapter 2, or Hamer's *Dictionary*. For more detail, see the list of references at the end of this chapter. However, for the purposes of this course, the following comments are adequate to carry on if you do not have access to such references.

Our glazes are made of minerals, and most minerals are by nature crystalline. If you heat a crystalline material until it melts, the regular and rigid arrangement of atoms that is present in the crystal breaks down to give a random and moving arrangement of atoms in the molten state. If the molten material is now cooled, crystals will usually re-form. However, the peculiarity of glasses and glazes is that they tend to retain the random arrangement typical of a liquid, when cooled at a normal rate. The atoms do not have time to re-form into crystals before the material has cooled to a solid mass. So, if you examine a glass microscopically, it has the appearance of a liquid, in spite of its solidity. This is why glazes and glasses are sometimes called 'supercooled liquids' — 'supercooled' referring to the fact that the material was cooled too fast for crystals to form, so the material remains 'vitrified'.

Many glazes have a tendency under some conditions to form crystals, however; and this process is sometimes

DIAGRAM 16.1



called 'devitrification'. Sometimes the crystals are large and dramatic, centimetres across; sometimes they are visible with a hand lens, giving a matt glaze; and in some glazes the crystals are so tiny that one needs an electron microscope to see them. These minute crystals, sometimes called 'crystallites', can be a source of opacity and some colours, in glazes.

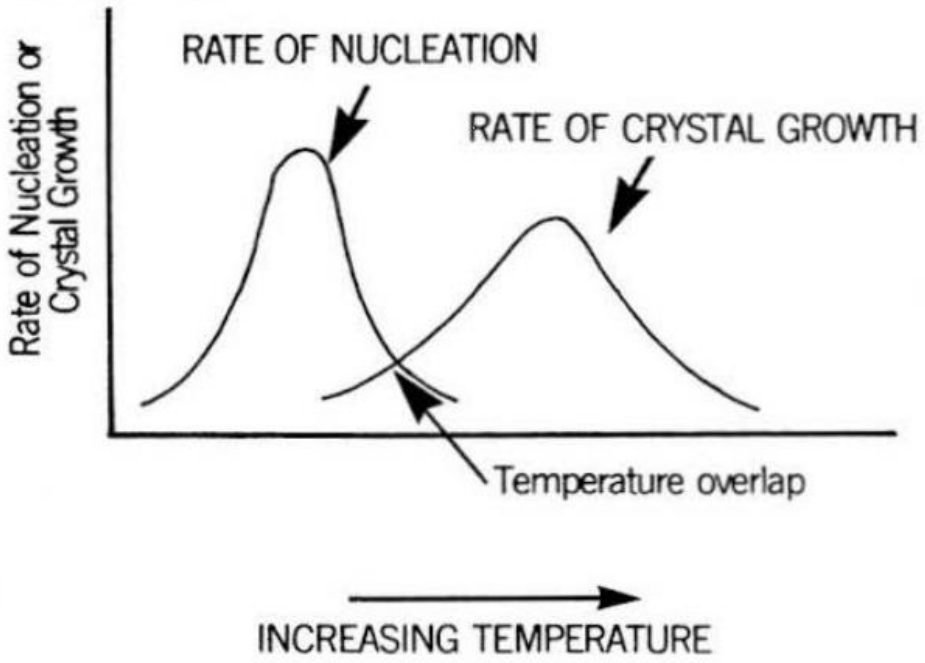
THE PROCESS OF CRYSTALLISATION

We must divide the process of crystallisation into two stages. Firstly, appropriate seeding points, or nuclei, on which the crystals can grow, must be provided. There are a number of ways of getting these nuclei, e.g. they may be a grain of silica left undissolved in the molten glaze or from the body at the clay/glaze interface, or one may artifically seed the surface of the glaze with a refractory material, or they may occur spontaneously by a process known as 'nucleation'. The second stage, crystal growth, can occur once the nuclei have been provided and the glaze is adequately fluid. The phenomenon of nucleation has been studied in some depth for copper red glazes and others and is well covered in Parmelee (pages 205-204 and pages 466-467). But in brief, if you look at Diagram 16.1, you will see that a particular temperature favours the formation of nuclei, and a higher temperature favours the actual growth of the crystals. The maturing temperature of the glaze will usually be higher still. The nuclei that form at the nucleation temperature tend to dissolve back into the glaze as the temperature rises, and in fact one can fire them out altogether so that unless other sources of nuclei are present, no crystals will form during the cooling. If a large number of nuclei remain at top temperature, the ultimate result will be masses of tiny crystals giving a matt glaze. If you want just a few large crystals, there is the problem of getting just a few nuclei left. (See later under 'Firing', 'Artificial Seeding', and 'Clay Body'. Also Parmelee, page 210, quotes Norton on the subject.)

If the glaze at maturity has no nuclei left, there is still the possibility of nuclei forming by nucleation in the cooling period. If the nucleation zone and the crystal growth zone overlap, then crystals can grow in the overlapping temperature zone because nuclei will start to form while the temperature is still high enough for crystal growth to occur. (See Diagram 16.2) If the nucleation zone is too far below the crystal growth zone, the possibility exists (in the cooling cycle) of cooling to the nucleation zone, then raising the temperature to the growth zone and holding temperature. This would have to be done by trial and error unless you have sophisticated apparatus at your disposal to enable you to detect the nucleation temperature.

Nucleation and crystal growth take time, and time is an important factor in controlling crystal growth. See 'Firing'.

DIAGRAM 16.2



IMPORTANT FACTORS IN CRYSTAL GROWTH

A. *Molecular Formula*

Specific examples are given later but here are a few general comments.

In the fluxes, low atomic weights favour crystals. In the alkalies, lithium (atomic weight 6.94) seems best, followed by sodium (23) and then potassium (39.1). In the RO group, Mg, Ca, Mn, Fe, Zn all favour crystals, while those with high atomic weights (e.g. Ba, Pb) do not.

In the R_2O_3 group, some oxides assist, and some retard crystal growth. Alumina (Al_2O_3) can hinder or prevent formation of crystals, so it is *absent* from many formulae or present in only small amounts (see Diagram 16.3). Adding alumina increases glaze viscosity, which has important effects on:

1. rate of formation of the crystals
2. their size
3. the flowing of the glaze coating and
4. the heat range of the glaze.

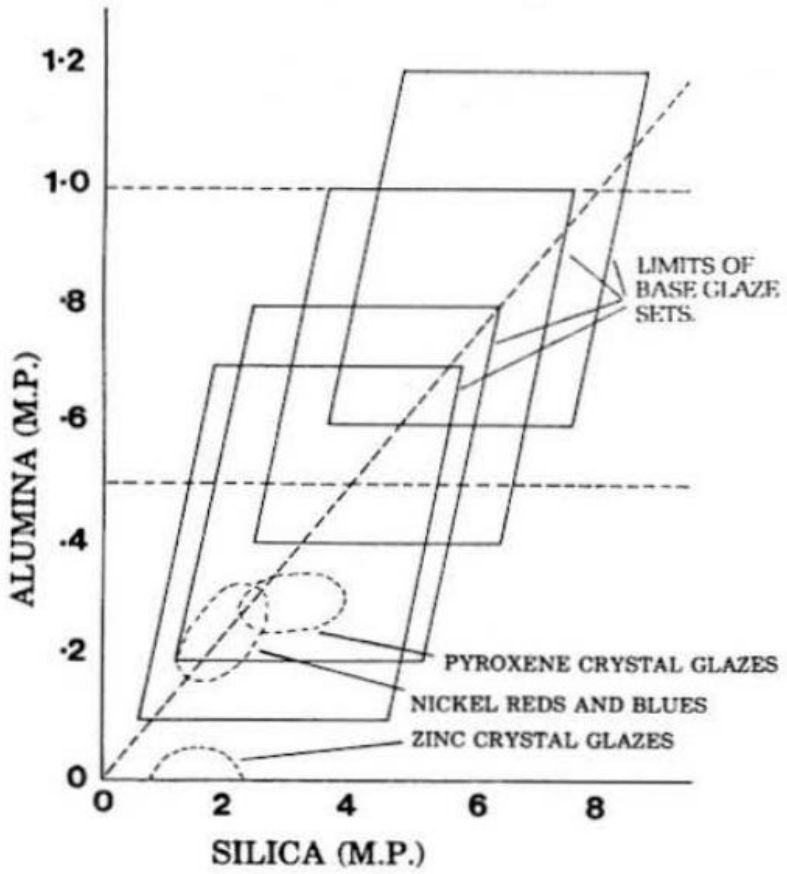
Therefore, manipulation of alumina content is an important factor in controlling crystal behaviour. A likely explanation of this important role played by alumina is as follows: In a complex mixture like a glaze, the crystals are rarely (probably never) of the same composition as the glaze itself, but represent a concentration in crystal form of only some of the glaze ingredients. This means that crystallisation 'in situ' (as one could imagine happens with water turning into ice) is not possible since a rearrangement or sorting of the atoms is necessary. So there is a need for the atoms to be able to diffuse through the glaze from the melt to the site of the crystal itself. Parmelee (page 465) says, . . . 'large crystals are possible only when the diffusion halo around the growing crystal can continue to be supplied with metal by diffusion from the parent glass.' This seems an adequate explanation for why low alumina, runny, highly mobile glazes favour growth of large crystals. The link between viscosity and diffusion is discussed under 'Viscosity', Parmelee, page 183 etc.

Boric oxide (B_2O_3) retards crystal growth, though it is often present in crystalline glazes, probably to aid maturity of a glaze at lower temperature.

In the RO_2 group, higher atomic weights favour crystals, e.g. Si, Ti, P.

Because of the requirement of low or zero alumina and a simultaneous need of alkalies, it is common in macro-crystalline glazes to resort to the use of frits, especially when trying for the very large

DIAGRAM 16.3
Illustrating the low values of Al_2O_3 and SiO_2 typical of crystalline glazes.



crystals. A possible way out of avoiding frits is to use lithium carbonate as your source of alkali, as long as this does not run you into shelling problems. A partially or fully fritted glaze will crystallise quite differently from an unfritted one of the same theoretical molecular formula. This is probably due to the difference in availability of seeding points. Methods of making your own frits are described in references by F.H. Norton, Cooper and Royle, and Herbert Sanders. (See References.)

Colouring oxide addition to the base glaze will usually provide interesting contrasts of colour between the crystals and the glass matrix because of their different compositions. Interesting examples are given later.

B. *Clay Body*

When trying for the large colourful crystals, one uses a fine white clay — white to emphasise the colours, and fine to avoid having masses of fine crystals grown from seeding points of sand or grog on the surface of the clay. Also, the forms are usually simple to provide a bland backdrop for the unimpeded growth of the crystals. This is not to say that you must avoid stoneware or rough clays or complicated forms; you may prefer the result.

C. *Firing*

For the large crystal types containing zinc, oxidation is essential.

To get large crystals, overfire the glaze to the point where it is literally running off the pot. This eliminates most of the unwanted nuclei but obviously presents a few problems. The end of the firing is usually done rapidly, hopefully to dissolve excess nuclei while not losing too much glaze. Michael Machtey (see References) applies excess glaze around the top of the pot, and most of it actually runs off the pot into a catcher. Do not apply the glaze thinly to prevent glaze run-off, or the crystals simply will not appear. Once top temperature has been reached it should be possible, and even desirable, to drop the temperature rapidly to the crystal growing temperature, which is commonly 100° to 200°C below top. The temperature is maintained at the desired level for perhaps 1 to 3 hours, then allowed to cool. Soaking at different temperatures produces different crystal types — it is possible to get different types of crystals from the same glaze by holding the firing at different temperatures on the way down, or even as a result of a natural cooling cycle. Machtey says, 'There seem to be quite a range of crystal sizes and patterns which can be obtained by varying the crystal growing portion of the firing schedule. This includes both raising as well as lowering the kiln temperature within the crystal growing range during this part of the schedule'.

Because of the problem of runny glaze, it is useful to consider here a few alternatives for catching the glaze runoff and separating the pot from its support. Some sort of strong saucer is necessary to hold the runoff, and some means of preventing the glaze from welding the pot onto the saucer must be devised. For example, a pedestal supporting the pot inside an unglazed footring may be used. (See Fig.1.) A wide bowl might have a conventional glaze outside (non-runny) and a crystalline glaze inside, with a small hole in the base allowing excess glaze to run through into a catcher bowl inside the raised foot. If the hole is reasonably small, the glaze will seal over. (See Fig.2). Another technique is to sit the pot squarely on the pedestal, which is coated with kiln wash, and the two are separated after the firing either by a sharp blow with a chisel, or by grinding the join back to the kiln wash (Fig.3). Some means of safely grinding the bases of pots is probably going to be necessary. *Be careful never to inhale powdered fired glaze.*

FIG. 1

FIG. 2

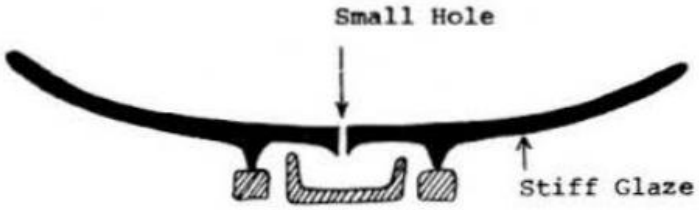
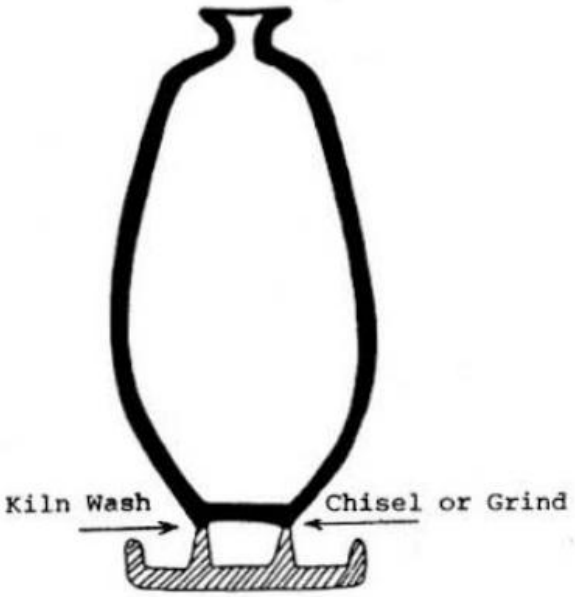


FIG. 3



Artificial Seeding

A number of ways of artificial seeding are possible. F.H. Norton in his article, 'Control of Crystalline Glazes' (*Journal of American Ceramic Society*, 20, Vol. 7, 1933), mentions successfully seeding with sodium carbonate (washing soda), calcium carbontate (whiting), zinc oxide and silica. Try applying 'seeds' where you want the crystals to grow.

DIFFERENT TYPES OF CRYSTALLINE GLAZES

According to Paul Rado (See References), 'The constituents capable of producing crystalline glazes are zinc silicate, zinc titanate, magnanese silicate, calcium and magnesium silicates. Tungsten trioxide (WO_3), vandium pentoxide (V_2O_5), and molybdenum trioxide (MoO_3) also produce crystals in glazes.' (*Note*: Zinc silicate would be produced from zinc oxide plus silica; zinc titanate from zinc oxide, titanium dioxide and silica, etc.) He is referring to macro-crystalline glazes, but I will include others here that are intermediate between the glazes giving really large crystals and those giving matt glazes.

1. *Zinc Silicate Crystals*

The fan-like crystals of Willemite ($2ZnO.SiO_2$), are responsible for some of the most dramatic of the macro-crystalline glazes. They form in glazes high in zinc and low in alumina and silica (alumina sometimes absent) e.g.:

*0.2 K_2O	2.0 SiO_2	Cone 12
0.8 ZnO	0.2 B_2O_3	

2. *Titanite Crystals*

Titanite ($CaO.TiO_2.SiO_2$) forms easily as small needlelike crystals, often giving just a matt. Titanite forms more readily than willemite, and may be developed with it in the same glaze coating. The TiO_2 should not be introduced as a frit.

3. *Pyroxene Crystals*

These crystals are small, though often easily visible, with a general formula of $RO.SiO_2$, where the R is probably mostly Ca and Mg. Two common forms of pyroxene found in stoneware glazes are Diopside ($CaO.MgO.2SiO_2$), and Augite, which is much the same, but with Fe, Al, and perhaps some KNa replacing some of the Ca and Mg. The crystals are usually small (1-3mm) but the effect is quite attractive, and the glazes are functional; whereas the zinc crystal glazes tend to be more decorative than functional, zinc silicate crystals being easily discoloured, and the low silica content making the glazes easily scratched. Pyroxene crystals will crystallise out of a large range of calcium glazes, including copper reds, tenmokus and other colour glazes, as long as they are reasonably low in alumina and contain a moderate amount of MgO. The following would be a typical base glaze for formation of such crystals:

* 0.2 KNaO		
0.6 CaO	0.25 Al_2O_3	2.5 SiO_2
0.2 MgO		

fired to about Cone 10. Pyroxene crystals are almost certainly responsible for the high silica matt opaque glazes around glazes 28, 29 in the Magnesium Set. The fact that the speckled (sometimes overall matt) effect of this crystal type can be superimposed on a wide range of glaze colours makes it a very useful addition to our growing collection of glaze phenomena.

4. *Aventurines*

If you like glitter, aventurines might be your thing. However, they are usually earthenware glazes, or mid-fire, and are well covered in other textbooks.

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* For more specific recommendations, including recipes, see the following section, 'Exercises'.

Aventurines are usually produced with iron oxide but have also been made using chromium, copper and uranium as the crystal producing agent. (See the text by Fraser, Chapter 12). A number of aventurine glaze formulae, most containing lead, are listed in Parmelee, Chapter 16, some firing as high as Cone 4. A lead-free Cone 4 aventurine is:

0.9 Na_2O	0.15 Al_2O_3	6.0 SiO_2
0.1 BaO	0.95 Fe_2O_3	2.0 B_2O_3

This particular glaze was entirely fritted.

5. *Zinc-Barium Silicate Crystals*
This sort of crystal is used to obtain reds and blues with nickel. Although there is zinc in the glazes, you do not get willemite but smaller crystals of a zinc-barium silicate, coloured red or blue by the nickel. The particular colour depends on the balance of zinc and barium oxides. These colours are very sensitive to conditions of firing and glaze composition. The crystal mineral is supposedly weak in acid, and sometimes the weather ... (this is from a Japanese text; in Japan they sometimes have very corrosive weather!) and therefore I cannot recommend their use on functional ware since they may come in contact with vinegar, fruit juice etc. The following formula is fairly typical:

*0.25 K_2O		
0.15-0.2 CaO	0.3 Al_2O_3	2.0 SiO_2
0.2-0.3 BaO		
0.4-0.25 ZnO	plus 0.15 *M.P.* NiO	

(From Reference No. 10)

6. *Raw Sodium Silicate Glazes*
Sanders mentions several raw sodium silicate glazes (Sodium Silicate = 'Water Glass'). He makes the following points:

a. these glazes need to be brushed on, not sprayed
b. they should be sieved through at least 60 mesh sieve and
c. they should be used immediately they are made up.

Some Recipes (Sanders):

a.	Sodium Silicate	50 C.C.
	Silica	20 Grams
	Zinc Oxide	18 Grams
	Titanium Dioxide	8 Grams
	Water	5 C.C.
b.	Sodium Silicate	50 C.C.
	Silica	25 Grams
	Zinc Oxide	25 Grams
	Titanium Dioxide	5 Grams

Try adding colouring oxides to these.

7. *Other Crystal Producing Agents*
The following materials will also promote crystal in Glazes:

Bismuth
Copper
Manganese } With Zinc
Cobalt
Tungsten
Molybdenum
Vanadium

Sanders' book has a section on Molybdenum crystals.

EXERCISES

The following is an assortment of formulae and recipes from different sources. Try some of them. (Note: Any frits listed are available in Australia.)

A. **Macro-Crystalline Glazes**

1. Michael Machtey — (Reference No.4)

Ferro Frit 3110	46	This recipe is based
Silica	21	approximately on the formula:
Zinc Oxide	27	
Titanium Dioxide	5	0.35 Na_2O 1.85 SiO_2
Alumina Hydrate	1	0.65 ZnO 0.2 TiO_2

Machtey recommends the following additions of colouring oxides, singly or in combination:

Cobalt Carbonate	0.2%—0.5%
Copper Carbonate	1%—4%
Iron Oxide (red)	1%—4%
Manganese Dioxide	1%—3%
Nickel Oxide (green)	1%—2%

He uses an electric kiln (zinc crystalline glazes need to be fired in oxidation), and a typical firing schedule is as follows:

1. 25°C to 900°C	3 to 4 hours
2. 900°C to 1265°C	2 hours (full power)
3. 1265°C to 1140°C	10 minutes (power off)
4. 1140°C	2 hours
5. 1140°C to 1080°C	10 minutes
6. 1080°C	2 hours

2. Herbert Sanders

a.	Ferro Frit 3110	52	To this base glaze, he recommends you add:
	Zinc Oxide	24.34	(a) Cobalt Carbonate
	Silica	23.66	(b) Manganese Dioxide
			(c) Copper Carbonate
	Fire to Cone 10, Oxidation.		
b.	Ferro Frit 3124	50.85	Try adding:
	Zinc Oxide	22.32	(a) Copper Carbonate
	Silica	26.83	(b) Manganese Dioxide
			(c) Red Iron Oxide
	Fire to Cone 10, Oxidation.		(d) Nickel Oxide (especially)
c.	Ferro Frit 3110	65	Try any colourant.
	Zinc Oxide	25	
	Silica	15	
	Fire to Cone 8 — 10, Oxidation.		

B. **Pryoxene Crystals**

1. Etsuzo Kado

The Japanese text by Mr Kado recommends that 2% or 3% bone ash is a useful addition in glazes developing pyroxene crystals. Starting with the following base glaze:

SEGER FORMULA (KADO):	OXIDE	WT%	TYPICAL RECIPES:	A	B	C
0.2KNaO	K_2O	8.0	K-FELDSPAR	40.7	40.7	41.7
0.18MgO $0.25Al_2O_3$ $2.5SiO_2$	MgO	3.1	KAOLIN	4.7	4.7	4.8
0.62CaO	CaO	14.7	SILICA	26.4	26.4	21.6
	Al_2O_3	10.8	WHITING	22.7	16.1	23.3
	SiO_2	63.5	MAG. CARB.	5.6	—	—
			DOLOMITE	—	12.1	—
			TALC	—	—	8.5

(Orton Cone 10), which he quotes as being a typical 'ash glaze' with small spots of crystals on the surface, he suggests you add 2% to 3% bone ash, plus a colourant, e.g. 1% CoO, 1% NiO, HIGH NiO, 7% Fe_2O_3 etc. to give interesting colour crystals. Remember that these crystals are fairly small, quite different from the zinc crystalline glazes; but in my experience, it is possible to develop masses of crystals completely covering the surface of the glaze with a pleasant matt finish of the colour of the crystal. I will discuss this technique when explaining the high-iron glaze known as 'Teadust' later.

2.

Another fairly typical base glaze giving well developed pyroxene crystals:

SEGER FORMULA	OXIDE	WT%	TYPICAL RECIPES:	A	B	C
0.1 Li_2O	Li_2O	1.4	Lithium Carb.	3.0	3.0	3.2
0.2 K_2O	K_2O	9.1	K-FELDSPAR	45.3	45.3	47.5
0.4 CaO $0.3Al_2O_3$ $2.0SiO_2$	CaO	10.8	KAOLIN	10.5	10.5	11.0
0.3 MgO	MgO	5.8	SILICA	14.7	14.7	5.1
	Al_2O_3	14.8	WHITING	16.3	4.1	17.1
	SiO_2	58.0	MAG. CARB.	10.3	—	—
			DOLOMITE	—	22.5	—
			TALC	—	—	16.2

C. **Nickel Reds and Blues**

1. Parmelee (Reference No.1)

The following two formulae are given in Parmelee, page 72, and are meant to be fired to about Orton Cone 6, oxidised:

SEGER FORMULAE (PARMELEE):	OXIDE	WT%	TYPICAL RECIPES	
BLUE				
0.25 K_2O	K_2O	9.5	K-FELDSPAR	52.5
0.14 CaO	CaO	3.2	WHITING	5.3
0.21 BaO 0.3 Al_2O_3 2.0 SiO_2	BaO	13.0	BARIUM CARB.	15.7
0.41 ZnO	ZnO	13.5	ZINC OXIDE	12.6
	Al_2O_3	12.3	KAOLIN	4.7
	SiO_2	48.5	SILICA	9.1
PURPLE				
0.25 K_2O	K_2O	9.4	K-FELDSPAR	50.5
0.20 CaO	CaO	4.5	WHITING	7.3
0.30 BaO 0.3 Al_2O_3 2.0 SiO_2	BaO	18.3	BARIUM CARB.	21.5
0.25 ZnO	ZnO	8.1	ZINC OXIDE	7.4
	Al_2O_3	12.1	KAOLIN	4.7
	SiO_2	47.7	SILICA	8.7

To each of these is added 0.15 M.P. of NiO.

(*Note*: There are two forms of Nickel Oxide, NiO (green), and Ni_2O_3 (black). However, Ni_2O_3 breaks down to give $2NiO + \frac{1}{2}O_2$ at 600°C.

To convert the 0.15 M.P. of NiO to a percentage, just put it up there with the other oxides listed under 'Required Glaze' (see Conversion Chart in Chapter 14) and make the conversion as usual. If you are using green NiO, M.Wt is 74.7, and if using black Ni_2O_3, M.Wt is 165.4, and remember that 1 M.P. of Ni_2O_3 will give you 2 M.P. of NiO in the fired glaze.)

2. Emmanuel Cooper (Reference No.5)

He quotes the following recipe as approximating to Parmelee's Blue (above):

Feldspar	52	
Whiting	5	He says: 'Increases in
Barium Carbonate	15	the amount of calcium
Zinc Oxide	12	and barium will give
China Clay	6	more purplish colours'.
Silica	10	
Nickel Oxide	2	

He gives the following recipe for 1250°C to 1280°C oxidation firing, for a matt pink/blue glaze:

Feldspar	35
Barium Carbonate	40
Zinc Oxide	15
China Clay	5
Silica	5
Nickel Oxide	1-3%

He suggests that firing temperature, glaze thickness, and body type are all important variables. The following recipe is given as a mottled green (tends to run) for 1250°C to 1260°C oxidation firing:

Feldspar	55
Whiting	10
Zinc Oxide	10
Barium Carbonate	20
Ball Clay	5
Nickel Oxide	2

3. Etsuzo Kado (Reference No.10)

The following two formulae are given by Mr Kado — you will note some important similarities to the two formulae of Parmelee's:

SEGER FORMULAE (KADO):	OXIDE	WT%	TYPICAL RECIPES	
BLUE				
0.20 KNaO 0.55 ZnO 0.05 CaO 0.2 Al_2O_3 1.7 SiO_2 0.20 BaO Plus 1-2% NiO	K_2O	8.6	K-FELDSPAR	48.3
	ZnO	20.4	ZINC OXIDE	19.4
	CaO	1.3	WHITING	2.2
	BaO	14.0	BARIUM CARB.	17.1
	Al_2O_3	9.3	KAOLIN	—
	SiO_2	46.5	SILICA	13.0
	NiO	1-2%	NICKEL OXIDE	1-2%
RED				
O.10 KNaO 0.40 ZnO 0.40 BaO 0.12 Al_2O_3 1.5 SiO_2 0.10 MgO Plus 1% NiO	K_2O	4.5	K-FELDSPAR	23.9
	ZnO	15.5	ZINC OXIDE	14.0
	BaO	29.3	BARIUM CARB.	34.0
	MgO	1.9	MAG. CARB.	3.6
	Al_2O_3	5.8	KAOLIN	2.2
	SiO_2	43.0	SILICA	22.2
	NiO	1%	NICKEL OXIDE	1%

Oxidation fire — temperature not given. Cone 7 — 9?
Remember the note of caution given about use of this type of glaze on functional ware. Also, the colours will be brighter on white stoneware or porcelain.

REFERENCES

1. *Ceramic Glazes* by Cullen W. Parmelee (Cahners Books)
2. *An Introduction to the Technology of Pottery* by Paul Rado (Pergamon)
3. *Ceramic Science for the Potter* by W.G. Lawrence (Chilton Book Company).
4. 'Crystalline Glazes' from *Ceramic Review 1/2* 1978 by Michael Machtey.
5. 'Nickel Glazes' from *Ceramic Review 1/2* 1979 by Emmanuel Cooper.
6. *Glazes for the Studio Potter* by Cooper and Royle (Batsford).
7. *Glazes for Special Effects* by Herbert Sanders (Watson/Guptill).
8. *Ceramics for the Artist Potter* by F.H. Norton (Addison- Wesley).
9. *Glazes for the Craft Potter* by Harry Fraser (Pitman).
10. *Fundamentals of Glazes* by Etsuzo Kado, (In Japanese).
11. *The Potter's Dictionary of Materials and Techniques* by Frank Hamer (Watson/Guptill).

For glass theory, see references 1, 2, 3 and 11. For techniques for frit making, see references 6, 7 and 8.

17 MATT GLAZES

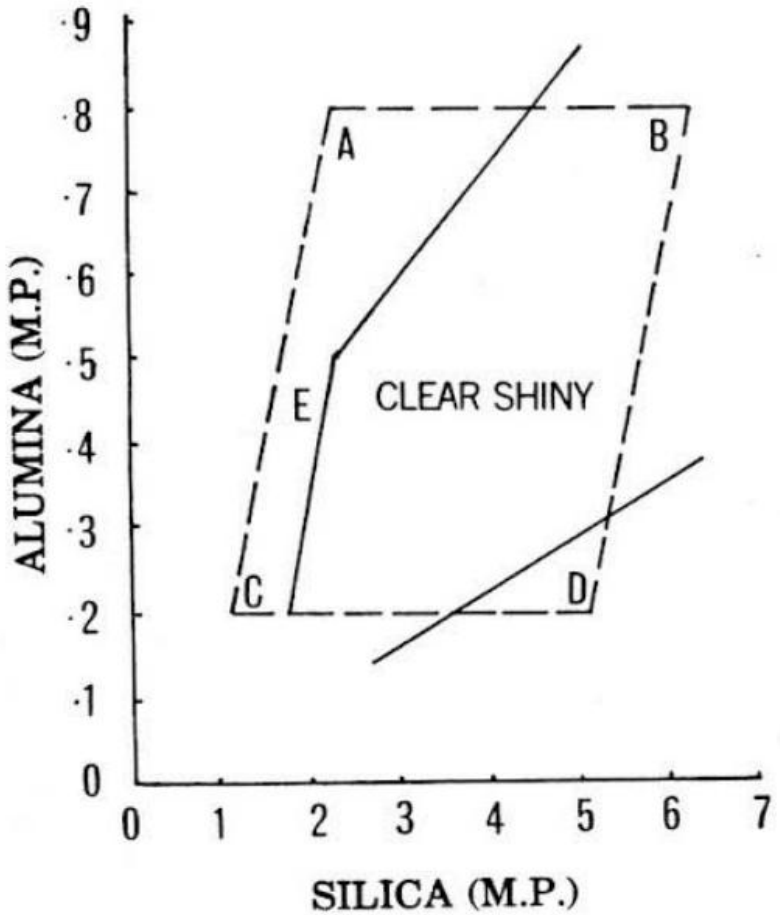
Mattness in glazes is due to the refraction and diffusion of light rays reflected from a surface that is minutely rough. This roughness may be caused by tiny crystals, undissolved materials, or by mechanical abrasion (e.g. sand blasting), or chemical corrosion (e.g. with hydrofluoric acid) or by bubble effects, or sometimes by minute crinkling of the glaze surface as it cools.

A number of different types of matt glazes were revealed with the systematic base glaze experiments (See Diagram 17.1).

In most sets, alumina matt glazes appeared around A, unless they were severely overfired. The different types (limestone, barium, magnesia) of alumina matts showed subtle differences. Often they appeared semi-opaque or translucent, rather than really white opaque.

In many sets, a kind of high-silica 'matt' appeared around D in a narrow band between the clear shiny glazes and the underfired glazes. These glazes were white opaque, often with a cold sugary surface, often rough to the touch. In the Magnesium Set and the 0.8 Limestone

DIAGRAM 17.1 : MATT GLAZES SURROUNDING THE CLEAR SHINY ZONE.



Set, however, there appeared a band of excellent white matt opaque glazes.

In many sets the combination of high alumina and high silica in area B makes the glazes slightly underfired and therefore slightly matt and semi-opaque. These glazes easily become clear and shiny at higher temperature.

A number of interesting matt glazes, including those usually referred to as calcium matts and barium matts, occur in the zone marked 'E'. Examples of these will be found in the Barium Set and the 0.9 and 0.8 Limestone Sets. Sometimes these glazes exhibit an interesting colour-break phenomenon, depending on glaze thickness, iron in the clay etc., and it is obviously evidence of the interaction of clay and glaze. (See 'The Clay-Glaze Interface' below.)

Corner C shows rather unstable glazes with a short firing range — sets fired to different temperatures easily produce immature or runny glazes. Large crystals form easily in this corner in some of the sets (e.g. 0.8 Limestone, Zinc and Magnesium Sets).

All this is leading up to a rather simple idea — if you move in any direction away from the 'clear shiny' zone, you will eventually overload the glaze with something that will cause mattness with the development of crystals, or because of the unmelted excess of whatever it is — in corner A, it is alumina in excess; in D, it is silica; in B, both alumina and silica; and in corner C, the excess is an overload of fluxes. The alumina/silica diagram, of course, accounts for only fluxes, alumina and silica; but you can eventually get mattness in glazes by overloading with almost anything, as long as the material on its own is refractory. The particular quality of mattness depends largely on which particular matting agent you choose.

THE CLAY - GLAZE INTERFACE

At stoneware temperatures there is usually a strong reaction between the glaze and the clay body, often forming a well-developed interfacial zone at the clay/glaze interface. This zone is usually, though not always, intermediate in composition and physical properties between the two layers. In many glazes, one can see a definite difference in glaze quality between where it is put on thin and put on thick. In a colour glaze, this might manifest itself as a colour break. These glaze differences can probably be explained as follows:

1. Sometimes crystal layers grow in the interfacial zone, and thin application of glaze brings this to the surface.

2. Conversely, some crystals form only when the glaze is thick — apparently alumina taken from the body retards crystal growth near the clay/glaze interface. This is the case with the magnesium opaque matts developing pyroxene crystals.

3. The thickness of glaze application is probably not going to affect the nature and extent of the interaction zone (unless the glaze is extremely thin) and so the same amount of material will diffuse into a thin layer as into a thick layer of glaze. Obviously, this will change the composition of the thin layer more than the thick.

4. Imperfect diffusion of the materials leached from the body would leave layers nearer the body richer in these materials and, in the case of matt glazes, which are more or less opaque, only the colour of the outer layer would be seen.

Let us look now at some of the factors that affect the clay/glaze interface:

a. **The Clay Body**

A body that is still porous when the glaze has completely fused will tend to absorb the molten glaze and react strongly with it. The same glaze melting onto a non-porous (i.e. vitrified) body will not intermingle with it so well, and the end result will probably be quite different. It is also apparently the case that the clay is more susceptible to attack by the glaze if the clay has not previously been bisque fired. (See Singer page 543.)

b. **The Glaze**

According to Singer, a common rule is that the lower the glaze is in alumina, the more it will attack the body. This is probably explainable in terms of the low alumina glazes having:

1. lower viscosity and
2. higher flux content.

Certain glaze ingredients such as lead, barium, boric oxide, lime and the alkalis, are very active in attacking the clay.

c. **The Firing — Time/Temperature**

The higher and longer the firing, the greater the interaction between clay and glaze.

d. **The Firing — Atmosphere**
Reduction of an iron bearing body will render the iron oxide to the ferrous form (FeO), which acts as a powerful flux in the body, as well as a colourant. This seems to be a factor in some colour-break glazes.

EXERCISES

Examine your base glaze tests for good matt glazes, and develop matt colour glazes from them by addition of colouring oxides and opacifiers. The following are a few specific suggestions, some occurring outside the limits of your base glaze tests. They can be divided into flux matts, alumina matts and silica matts, depending on what is used to produce the mattness. There is no sharp line between the different types — one merges into another as you move around the borders of the clear shiny glaze region.

1. Flux Matts

Because of their low alumina and silica content, these glazes are rather unstable and somewhat unpredictable, but philosophically I find that one hundred per cent predictability equates with one hundred per cent boredom ... press onwards!

a. *Flux Addition by Line Blend*

An easy way to produce flux matts is to take almost any glaze that is already low in alumina and silica and add more and more of some particular RO flux to it, e.g. ZnO, BaO, CaO, MgO. For example,choose any glaze that melts in the zinc or barium or 0.9 or 0.8 Limestone or Magnesium Sets around Corner C (the high flux corner), and do a line blend from that glaze to a 'glaze' that has, say, 50% of the added RO flux, e.g. barium carbonate, whiting etc. Try 10 steps (5% additions). This is a crude but effective way of producing matt and dry glazes. Some of the glazes may be very runny. Use varied thickness, varied clay bodies, and apply stripes of colouring oxides. Use any clay bodies you like but have some variety, e.g. Walker's No.9 (dark, iron-rich stoneware) and Walker's No.10 (white stoneware) should give an interesting contrast.

b. *Barium Matts*

(i) In the Barium Set done in Part I, investigate more fully glazes numbers 11, 12, 16, 17, 21 and 22. Apply them with varying thickness to 'individual tiles', or even pots, trying different clays and applying colouring oxides as mentioned above. If you have done Part I, you will have already prepared the glazes by volumetric blending — if not, you will find the individual recipes in the Barium Set Data Sheet (see Page 77). If you feel like doing a little adjustment, you could increase the BaO at the expense of the CaO — it is not uncommon to go as high as 0.7 M.P. BaO. (See later under 'Various Recipes'.) *Until more is known about barium release from this type of glaze, I cannot recommend these glazes for use inside functional pots.*
(ii) Kado suggests the barium matt glaze shown in the data box for use on functional ware.

He comments that the barium matts are translucent and textured compared with zinc matts, which are opaque and untextured.

He suggests the following additions to the glaze:
CuO 1-2%.
Cr_2O_3 1%.
MnO_2 5%.
Fe_2O_3 6%.
CoO 1%.
NiO 2%.

He suggests you also try adding some opacifier with the colouring oxide additions. (Rutile will give some interesting textured matts — try 3% to 6%.)

(iii) Various Recipes
Make up the following recipes from various sources, varying body, thickness of

KADO'S BARIUM MATT GLAZE

SEGER FORMULA (KADO):	OXIDE	WT%	TYPICAL RECIPE	
0.2 KNaO	K_2O	7.6	K-FELDSPAR	38.5
0.5 CaO 0.35 Al_2O_3 2.0 SiO_2	CaO	11.3	WHITING	17.3
0.3 BaO	BaO	18.5	BARIUM CARB.	20.5
	Al_2O_3	14.3	KAOLIN	13.4
	SiO_2	48.3	SILICA	10.4

BARIUM MATTS

	Recipe	Base Glaze	Seger Formula	Oxide Wt%
(a)		$KNaO$	0.3	11
	Nepheline Syenite 50] Base	BaO	0.7	42
	Barium Carbonate 50] Glaze (a)	Al_2O_3	0.33	13
	Copper Carbonate 1.5%	SiO_2	1.43	34
	(Bentonite 3)	(Bentonite excluded)		
	Ref. No.4.			
(b)	Feldspar 45	$KNaO$	0.26	9
	Barium Carbonate 45	BaO	0.74	40
	China Clay 10	Al_2O_3	0.36	13
	Copper Carbonate 2	SiO_2	1.83	38
	Ref. No.4.			
(c)	Base Glaze (a) 100			
	Nickel Oxide 0.5%			
	(Bentonite 3)			
	Ref. No.4.			
(d)	Barium Carbonate 25	$KNaO$	0.39	12
	Nepheline Syenite 55	Li_2O	0.18	1.7
	China Clay 8	BaO	0.43	21
	Silica 8	Al_2O_3	0.54	17
	Lithium Carbonate 4	SiO_2	2.56	48
	Copper Carbonate 2%			
	Ref. No.4.			
(e)	Barium Carbonate 26	$KNaO$	0.28	8.9
	Silica 20	CaO	0.14	2.6
	China Clay 10	MgO	0.14	1.9
	Feldspar 46	BaO	0.44	23
	Dolomite 8	Al_2O_3	0.4	14
	Cobalt Carbonate 1.5%	SiO_2	2.5	50
	Rutile 3%			
	Ref. No.4.			
(f)	Feldspar 62	$KNaO$	0.37	12
	Barium Carbonate 38	BaO	0.63	32
	Copper Carbonate 4%	Al_2O_3	0.37	13
	(Plus Rutile)	SiO_2	2.2	44
	See de Boos No.145			

CALCIUM MATTS

	Recipe		Base Glaze	Seger Formula	Oxide Wt%
(a)	Feldspar	33	KNaO	0.15	7
	Whiting	33	CaO	0.85	23
	China clay	33	Al_2O_3	0.49	24
	+ colouring oxides		SiO_2	1.59	46
	Ref. No.2. (see Glaze No.136)				
(b)	Feldspar	60	KNaO	0.35	12
	Whiting	20	CaO	0.65	13
	China clay	20	Al_2O_3	0.6	21
	+ colouring oxides, e.g.:		SiO_2	2.6	54
	(1) 2% Fe_2O_3 (+2% Rutile)				
	(2) 8% Fe_2O_3 (+2% Rutile)				
	(3) other colourants				
	Ref. No.4.				
(c)	Calcium alumina matt	1:	RO	1.0	
	Whiting	45	Al_2O_3	0.45	
	China clay	45	SiO_2	1.0	
	Ballclay	10		(approx.)	
(d)	Calcium alumina matt	2:	KNaO	0.02	1.2
	Whiting	45	CaO	0.98	34
	China clay	45	Al_2O_3	0.4	25
	Feldspar	5	SiO_2	1.06	40
	Silica	5			
	Add colouring oxides to (c) and (d), fire in oxidation or reduction, 1250°C to 1280°C. Ref. No.4.				
(e)	Feldspar	4	KNaO	0.02	1
	Whiting	31	CaO	0.89	25
	China clay	40	MgO	0.1	2
	Silica	18	Al_2O_3	0.41	21
	Dolomite	7	SiO_2	1.66	50
	Add colouring oxides. Fire in reduction or oxidation. A glaze used by Eileen Lewenstein quoted in Ref. No.4.				

application, firing etc. (most are meant for oxidation). The reference source is given with each recipe. I have calculated approximate figures for Seger Formula and Oxide Wt % for the base glaze in each case, i.e. excluding colouring oxides and rutile.

See the table: BARIUM MATTS

c. *Calcium Matts*

(i) You will find a number of excellent calcium matt glazes in the base glaze exercises done in Part I in the 0.9 and 0.8 Limestone Sets. Investigate more fully the following glazes: In the 0.9 Limestone Set, Glazes 6, 7, 11 and 12, and in the 0.8 Limestone Set, glazes 6 and 11. Apply them with varying thickness to 'individual tiles' or pots, trying different clays and applying colouring oxides as previously suggested for the barium matts. If you have not already done Part I, you will find the recipes for the glazes mentioned above listed in the relevant Data Sheets.

(ii) *Various Recipes*

Make up the recipes (see the Table: CALCIUM MATTS) taken from various sources and vary body, thickness of application, firing etc. The reference source is given for each recipe. I have calculated approximate figures for Seger Formula and Oxide Wt % for the base glaze in each case, i.e. excluding colouring oxides and rutile.

2. **Alumina Matts**

All the base glaze sets at appropriate firing temperatures exhibit alumina matts around Corner A. There are a number of very rich matts in this area in the Barium Set and the Magnesium Set, e.g. in the Barium Set, glazes nos. 8, 12, 13, 17; and in the Magnesium Set, glazes 1, 2, 3, 6, 7, 8, 11, 12. On the basis of the results from Part I, choose a few good alumina matts and test them further, including the use of colouring oxides to develop some colour matt glazes. If you have not done the exercises in Part I, you could use the Results Charts (for the Barium and Magnesium Sets) for guidance and get the individual recipes from the appropriate Data Sheets.

Kado suggests zinc alumina matts as being useful for developing pleasant colour glazes. He suggests the alumina matt shown in the data box.
He says it is useful for lower temperatures, eg. Orton Cone 7, 8, but the glaze becomes clear and shiny at higher temperatures. (See your Zinc Set of base glazes, which has almost identical fluxes). The colour responses will be different from the barium matt and the magnesium matt glazes. (Some people find them a little bland, typically pastel, untextured opaque colour glazes.) Kado suggests the following colour additions: Fe_2O_3 5%; CoO ½-2%; NiO 1%, 3%; Cr_2O_3 ½%; CuO 1%. He also suggests addition of opacifiers such as TiO_2, SnO_2, ZrO_2 and bone ash. (Try 2% to 4%).

3. **Silica Matts**

These are not as universal as the alumina matts; for example, they do not seem to occur in the Barium Set or the Zinc Set. However, they are apparent in the Magnesium Set and the high-limestone sets, especially the 0.8 Limestone Set. The effect does not seem to develop if the glazes are fully matured; however, there is more to the mattness than just undissolved silica in an immature glaze. Draw trials show that the mattness and opacity evident in the Magnesium and 0.8 Limestone Sets in this region (e.g. glazes 29 and 33 in Firing No.2 in either set) result from crystals forming in the cooling cycle. The crystals are presumably wollastonite ($CaO.SiO_2$) and, in the Magnesium Set, diopside crystals as well ($CaO.MgO.2SiO_2$).

KADO'S ZINC ALUMINA MATT

SEGER FORMULA (KADO):	OXIDE	WT%	TYPICAL RECIPE	
	K_2O	7.0	K-FELDSPAR	37.5
0.2 KNaO	CaO	8.3	WHITING	13.5
0.4 CaO 0.45 Al_2O_3 2.5 SiO_2	ZnO	12.1	ZINC OXIDE	11.0
0.4 ZnO	Al_2O_3	17.0	KAOLIN	21.8
	SiO_2	55.7	SILICA	16.2

Exercise: Explore magnesium silica matts using the following sources as a guide.

a. Refer to fired results you have obtained with the Magnesium Set in part I... or
b. If you have not done Part I, use the Results Charts as a guide, and obtain the individual recipes from the Data Sheet. Try glazes 29 and 33 and others in that area.
c. Kado (see Ref. No.3) suggests the magnesium silica matt shown in the data box, which will require a higher firing than some of the others.

Adding cobalt oxide (1%-5%) to these glazes will give purples and lilacs, and iron oxide will give golden yellows (1%-2%) or browns (5%+). The source of magnesia will have quite an effect on the quality of the glaze since some have considerable impurities.

Exercise: Explore limestone silica matts using either fired results from Part I or the Results Charts for the high-limestone sets as a guide. Try around glazes 29 and 33 in the 0.8 Limestone Set. Note that the Kuan-type glazes in the 0.6 Limestone Set fall into this category.

REFERENCES

1. *Industrial Ceramics* by Singer & Singer.
2. *Glazes for Australian Potters* by J. de Boos (Cassell Australia).
3. *Fundamentals of Glazes* by Etsuzo Kado (in Japanese).
4. *Glazes for the Studio Potter* by E. Cooper and D. Royle (Batsford).
5. *Glazes for Special Effects* by H.H. Sanders (Watson/Guptill).

KADO'S MAGNESIUM SILICA MATT

SEGER FORMULA (KADO):
0.15 KNaO 0.3 CaO 0.25 Al_2O_3 4.5 SiO_2 0.55 MgO

OXIDE	WT%
K_2O	4.1
CaO	4.8
MgO	6.4
Al_2O_3	7.3
SiO_2	77.5

TYPICAL RECIPES:	A	B	C
K-FELDSPAR	21.4	21.4	22.6
KAOLIN	6.6	6.6	7.0
WHITING	7.7	—	8.1
MAG. CARB.	11.9	5.4	—
SILICA	52.4	52.4	43.4
DOLOMITE	—	14.2	—
TALC	—	—	18.8

18 OPAQUE GLAZES CHUN-BLUE GLAZES

Opacifiers are well covered in many basic texts, such as Reference Nos 1 and 2 (by Fraser and Hamer) that I recommend you read. I will just give the bare essentials here before treating in detail some of the more important and interesting types of glazes involving opacity. Opaque glazes and Chun-blue glazes are discussed together here because they are caused by the same phenomenon. Opacity is the result of interference to light rays inside the glaze or at the surface. Chun-blue glazes are a type of semi-opaque glaze resulting from light interference inside the glaze. In both cases, the interference of the light rays is caused by tiny particles suspended within the glaze. The particles are of several kinds:

1. Suspended crystalline particles that do not melt as the glaze melts, e.g. tin oxide, excess silica etc.

2. Crystalline particles that crystallise out of the molten glaze, e.g. TiO_2 crystals, and crystals caused by use of excess CaO, BaO, ZnO, MgO, Al_2O_3 etc.

3. Colloidal particles, e.g. minute bubbles caused by sulphur, fluorine or chlorine in a glaze, and also the type of colloid that forms on cooling when you have two immiscible glass phases such as phosphate and silicate glasses.

4. Bubbles of any kind, as long as they are fine enough (preferably not visible to the naked eye).

OPAQUE GLAZES

Most texts discuss opaque glazes simply in terms of adding an opacifier (e.g. tin oxide) to a glaze and then leave the subject at that. There are, however, many different types of opacity, some whiter than others, some textured, some shinier than others etc., and you need to be familiar with the various kinds.

I usually use the term *opaque* in a purely descriptive sense. Here I am using it as a way of classifying a certain group of glazes, namely *shiny* opaque glazes, and ask you to keep these separate in your mind from 'matt glazes', which are *necessarily* opaque or semi-opaque, and which are dealt with in the previous chapter.

Matt glazes of many types have enjoyed popular appeal for some time, but not much is written in texts about shiny opaque glazes. Perhaps the shiny, rather paint-like, quality has come to remind us of the worst of mass-produced ceramics, which makes extensive use of this type of glaze. Mere materials are never 'good' or 'bad', however, it is what you do with them that counts, and I would be surprised if you cannot find some use in your palette of ceramic colours and effects for this type of glaze. The following are several approaches to developing shiny opaque glazes.

1. SIMPLE ADDITION OF OPACIFIERS

Take any shiny base glaze (from your sets or elsewhere) and add progressive amounts of several opacifiers in a series of line blends. Glaze a set of individual tiles and apply some colouring oxides in the same way as for the base glaze sets; but remember to leave, say, half the tile free of colouring oxide to get a good clear view of the opacified glaze by itself.

The following opacifiers should be useful in this comparative exercise:

tin oxide, zircon (use opacifier grade, e.g. MZS3, from Russell Cowan), titanium dioxide, bone ash.

In each line blend, have opacifier additions of 2½%, 5%, 10% and 20%, and

fire a couple of samples of the glaze without opacifier. If you are working on your own or in a very small group, it may be quicker to use the mortar and pestle line-blending technique, described at the beginning of Part II.

Compare the quality and effectiveness of the different opacifiers. Observe effects that they have on shine, melting point, glaze faults such as bubbling, pinholes, crawling etc. and on the colouring power of any colouring oxide used.

Theoretically, opacifiers will work most effectively in a zinc glaze, least effectively in a barium glaze.

Note: Large additions of zircon ($ZrO_2.SiO_2$) will put significant extra silica into the glaze, and theoretically one should compensate (to maintain level of glaze maturity) by addition of alumina and/or fluxes (e.g. ZnO). It should be possible to choose a shiny glaze that is relatively high in alumina such that successive additions of zircon do not unduly stiffen the glaze. I would recommend a shiny glaze with an alumina/silica ratio of around 1:5 or 1:6.

A Brief Comparison of Four Opacifiers

Many of these points will become evident in the tests suggested above:

Tin oxide
In spite of the expense, tin oxide is still the most popular opacifier in use with studio potters because of the soft creamy quality of the whiteness and the clean colours it produces in oxidation. However, it does not react favourably to reduction, giving an 'unpleasant grey cloudiness' to the glaze (Ref. Hamer p.299). It also is subject to 'chrome flashing' caused by vaporised chrome if there are even small amounts of chrome in the kiln. This effect produces pinks and reds, the pink usually having a particularly 'toilet-bowl' quality to it. A chrome red is discussed later.

Zircon
This works fine in reduction, does not suffer from chrome flashing, and is much cheaper than tin oxide. The quality of the opacity is a harsher white than with tin, however. But if you habitually use reduction, a suitable opacifier grade of zircon may be most suitable.

Bone ash
This is never pure calcium phosphate and will often produce greys and browns in a glaze. It can also be responsible for bubbles, or even blistering, and sometimes crawling. It is nevertheless worth trying. Bone ash samples can vary considerably.

Titanium dioxide
TiO_2 will pick up colour from the body, particularly iron, giving creams instead of whites. Also, it tends to produce matt opaques, rather than shiny, because of crystal formation. This also can cause mottling of colours. Most opacifiers tend to subdue colour in a glaze; this is particularly so with TiO_2.

2. USING AN OPAQUE BASE GLAZE

Select a shiny base glaze from your sets that is already opaque or showing signs of opacity (including milkiness or Chun-blue effect). If necessary, add an opacifier to produce full opacity.

Add colouring oxides to produce a range of opaque colour glazes. See below for some suggested combinations of colouring oxides. These combinations can be used in all types of glazes, but the results will depend very much on the type of base glaze. The comments are to give only a rough guide to what you can expect in oxidation. (Taken from Reference No.5.)

a. CuO (2%-5%) plus CoO ½% or less should give a light blue green in oxidation.
b. Fe_2O_3, 5%-6% + CoO, less than 1%, yellow green.
c. CoO, 1%-2% or more + MnO_2, 3%-5%, purple.
d. CoO + MnO_2 + Fe_2O_3 in relatively large amounts will give black.
e. Add MnO_2 to Fe_2O_3 to give different qualities of honey, from yellow brown to red brown.
f. Cr_2O_3 plus CoO will give a green blue opaque glaze.
g. Cr_2O_3 plus Fe_2O_3 — see red brown glaze later.
h. Cr_2O_3 plus MnO_2, chocolate opaque glaze.
i. Cr_2O_3 plus NiO.
j. NiO plus CoO. The nickel tones down the cobalt.

Where percentages are not quoted above, you could refer to a basic text such as Ref. 1, Chapter 11, for a rough guideline.

3. OTHER OPAQUE COLOUR GLAZES

Spinel Colourants

One family of colourants in ceramics is based on coloured spinels. This type of colourant is very stable, and many commercial ceramic colours are of this type. I will not go into preparation of spinel colourants; this is covered in texts on industrial ceramics, such as Parmelee and also Singer and Singer (See References). However, there are a number of spinel colours that will form in the glaze during the firing and, therefore, do not require any special preparation. Some are listed below.

The general formula for spinel is $RO.R_2O_3$, and rarely $2RO.RO_2$. Oxides commonly found in spinels are as follows:

A	B	C
ZnO	Al_2O_3	TiO_2
MgO	Cr_2O_3	SnO_2
MnO	Fe_2O_3	
CoO		
NiO		
FeO		

(Taken from reference no. 5, by Kado.)

Well-known examples of spinels are:

a. $FeO.Fe_2O_3$ (i.e. Fe_3O_4, Magnetite).
b. Chrome-tin pinks and reds, and according to Kado, the opacity in Bristol glazes is due to zinc spinel, $ZnO.Al_2O_3$.

Within each of the three groups, A, B and C, the oxides are interchangeable; and several may occur together, as long as the basic proportions of $RO.R_2O_3$ or $2RO.RO_2$ are maintained. The following list, again from Kado, shows some representative spinel combinations and their possible colours. Elements inside parentheses are interchangeable.

a.	$ZnO.(Al, Cr, Fe)_2O_3$	Yellow Brown, Red Brown
b.	$Zn, Co (Al, Cr)_2O_3$	Blue Green
c.	$(Zn, Co, Mn)O.(Cr, Fe)_2O_3$	Black
d.	$NiO.Cr_2O_3$	Green
e.	$MnO.Cr_2O_3$	Brown

Zinc is important in many spinel colours, and spinel colours form easily in zinc glazes.

Chrome is a strong spinel former and will form a number of opaque spinel colours in the right glazes. The following, taken from Kado, are examples of chrome being used as an opacifier and spinel type colourant:

(i) *Red Brown Opaque Glaze*

SEGER FORMULA (KADO):	OXIDE	WT%	TYPICAL RECIPE	
0.25 KNaO 0.35 ZnO 0.40 CaO 0.30 Al_2O_3 2.50 SiO_2	K_2O	9.2	K-FELDSPAR	50.7
	ZnO	8.8	WHITING	14.6
	CaO	11.2	ZINC OXIDE	10.4
	Al_2O_3	12.0	KAOLIN	4.7
	SiO_2	58.9	SILICA	19.7
Plus 5% Fe_2O_3 0.5-2.0% Cr_2O_3	Fe_2O_3	5%	RED IRON	5%
	Cr_2O_3	0.5-2.0%	CHROME OXIDE	0.5-2.0%
Orton Cone 7-9?? OXIDATION				

(ii) *Other Colouring Oxides in Combination with Chrome*

SEGER FORMULA (KADO):		OXIDE	WT%	TYPICAL RECIPE	
0.10 Li_2O		Li_2O	1.1	LITHIUM CARB.	2.4
0.13 KNaO		KNaO	4.3	K-FELDSPAR	23.0
0.38 CaO	0.32 Al_2O_3 2.9 SiO_2	CaO	7.6	WHITING	12.1
0.10 BaO		BaO	5.4	BARIUM CARB.	6.3
0.29 ZnO		ZnO	8.4	ZINC OXIDE	7.5
		Al_2O_3	11.6	KAOLIN	15.6
Orton Cn 7 OXIDATION		SiO_2	61.7	SILICA	33.2

To 100 parts of the above glaze, add 1 to 2 parts of Cr_2O_3 plus 5% Fluorspar, plus any of the following:

MnO,	6%
or Fe_2O_3,	6%
or NiO,	3%
or CuO,	4%
or CoO,	2%

Fluorspar:
Calcium fluoride (CaF_2)

(iii) *Chrome Red Glaze*

According to Kado, it is very important to choose the base glaze carefully for a chrome red glaze. He suggests the following as a starting point:

SEGER FORMULA (KADO):		OXIDE	WT%	TYPICAL RECIPE	
0.10 Li_2O		Li_2O	1.1	LITHIUM CARB.	2.3
0.15 KNaO		K_2O	5.0	K-FELDSPAR	25.6
0.58 CaO	0.28 Al_2O_3 3.0 SiO_2	CaO	11.4	WHITING	17.8
0.17 BaO		BaO	9.2	BARIUM CARB.	10.3
		Al_2O_3	10.0	KAOLIN	10.3
Plus	0.3% Cr_2O_3	SiO_2	63.4	SILICA	33.9
	6-7% SnO_2	Cr_2O_3	0.3%	CHROME OXIDE	0.3%
Orton Cn 10 OXIDATION		SnO_2	6-7%	TIN OXIDE	6-7%

He suggests the following variations to obtain best results:

1. Vary Al_2O_3 and SiO_2, by 0.05 M.P. and 0.5 M.P. steps respectively. In particular, take the figures as low as the materials will allow.
2. Chrome: 0.1% should give pink; 0.3% should give the best red.
3. Tin: He suggests that a whole range of colours may be had by varying SnO_2 between 4% and 10%.
4. The barium plays an important role. Vary between 0.17 and 0.08 M.P.
5. MgO and ZnO are apparently undesirable.

CHUN-BLUE GLAZES

THE CHUN-BLUE EFFECT

If you start with the right sort of clear glaze and modify it in the right way, you will achieve an opalescent blue glaze that I will refer to as 'Chun-blue'. Further modification of the same sort will turn the opalescent glaze opaque. This rather abstract statement is necessary because the 'modification' can be any or several of a number of factors, e.g. the addition of an opacifier and/or the adjustment of alumina/silica proportions, and/or adjustment in firing temperature and kiln atmosphere etc. Basically, the 'modification' we are talking about is the opacification of the glaze to the point where we have a special kind of semi-opaque glaze that gives the Chun-blue effect; and a number of factors can bring about this semi-opacity, including those mentioned above. Only a small minority of 'semi-opaque' glazes give Chun-blue. The critical factor is the *size of the particles* causing the opacity.

To understand this, See Diagram 18.1 and consider the effect of gradually decreasing the size of the particles of the opacifying agent. Remember that opacity is caused by the random reflection of white light off the opacifying particles.

Up to a point, the finer the particle size of the opacifying agent, the better it works as an opacifier. This is true, however, only so long as the particles are larger than the wave length of visible light. From the diagram, you will see that the wavelength of visible light is between 0.7 microns (red) and 0.4 microns (violet). Once the particles of the opacifying agent are significantly smaller than this, they are no longer able to reflect the light; and so the light will pass straight through. In this case, the glaze is transparent. In between the two extremes of

1. all light being reflected (opaque) and
2. all light going through (transparent),

you have the case where the particles are just the right size to let the coarser wavelengths (red) pass through, but reflect the shorter wavelengths to give the Chun-blue effect. It is usual to have a dark body (or slip or glaze) under the glaze. One function of this is to absorb the longer wavelengths that do pass through. If they are not absorbed but reflected by a pale body, the Chun-blue will to some extent be neutralised as the two ends of the colour spectrum recombine to give white again. The critical size of the particles is an academic point about which a certain degree of controversy exists. Cardew claims (see References) that Chun glazes are caused by suspended particles where the majority of these particles are of the range 0.45 to 0.5 microns. Parmelee says (page 215):

> 'One kind of opal glass may be considered as due to the presence of solid particles having diameters of the order of 1.3 microns, the average being very much less. The size will depend on the cooling rate and the viscosity of the glass.'

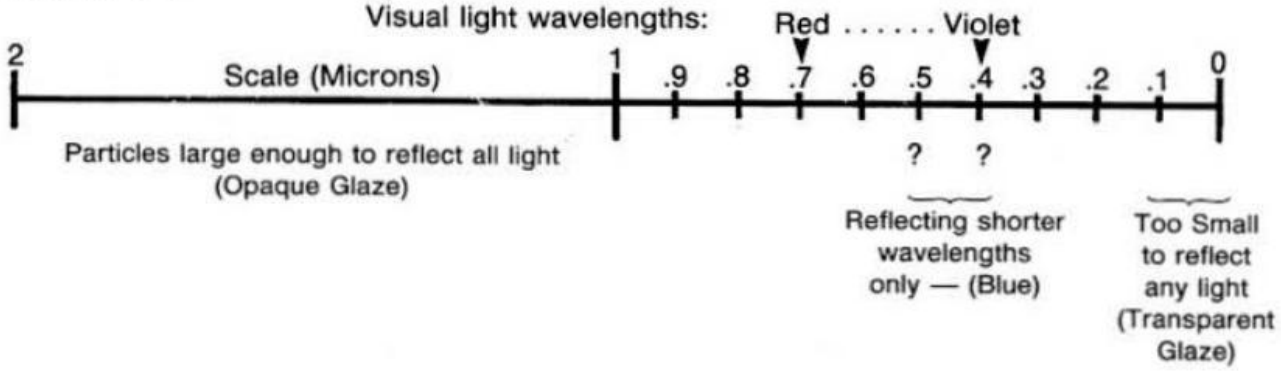
But it is not important that you know the exact size — what you need to realise is that there is a kind of threshold effect, a delicate balance between one state (opacity) and another (transparency), and you need to know ways of crossing this threshold. Then with an understanding of the principles that I am about to detail, you will be able to make the necessary adjustments to achieve the result you require.

FACTORS AFFECTING THE DEVELOPMENT OF CHUN-BLUE IN A GLAZE

1. Proportions of Alumina and Silica

In several of the sets of base glazes examined in the first half of this course, Chun blues were produced in the area marked on Diagram 18.2 as long as the glazes were fired high enough. The zinc

DIAGRAM 18.1



set probably produced Chun blues most easily, followed by the Limestone and Magnesium Sets. The interesting thing, however, was the consistency with which the blue zone appeared in the same area sometimes extending diagonally as shown in Diagram 18.2.

Analysis of a large number of Chun-blue glazes shows a remarkable consistency in this: *Low* alumina and silica, and the alumina/silica ratio around 1:12 (see examples later).

The actual form of the silica will sometimes affect the quality of the Chun-blue. Bernard Leach in *A Potter's Book* recommends the use of colloidal silica in Chun glazes, this being obtained, he points out, from grass ash and wood ash. Of course, these wood ashes will most likely introduce phosphorous as well, which is also a promoter of Chun-blue, but there is plenty of evidence to prove that colloidal or superfine silica is better for Chun blues than, say, normal 200 mesh mineral silica. Some sources of colloidal or superfine silica are as follows:

a. Vegetable ash, especially grasses, e.g. rice straw ash, rice hull ash, bamboo ash, sugarcane ash etc.
b. Any form of 'opal', e.g. diatomite, opal potch etc.
c. Industrial colloidal silica.
d. 400 mesh mineral silica.

In Japan it is traditional to use rice straw ash in Chun glazes.

2. Fluxes

As mentioned before, many of the base glaze sets produced Chun blues under some conditions. High barium, however, seems to prevent the effect occurring. The more alkaline of the lime-alkali glazes (0.6 Limestone and 0.6 Feldspar Sets) did not show any real Chun-blue on porcelain assessment tiles — presumably alumina is too high. Tests done with a highly alkaline set of glazes, using Podmore's Frit P.2250 as the only flux (0.5 Na_2O, 0.3 K_2O, 0.2 CaO), show that such glazes will produce the Chun-blue in the zone indicated on Diagram 18.2, so a wide range of flux combinations will produce the effect. All seem to have lime and alkalis, but beyond that, the picture is less clear. Zinc oxide seems to promote Chun blues; this ties in with its role as an opacifier. However, zinc is absent in traditional Chinese Chun glazes. In the Zinc Set, the effect sometimes occurs well beyond the zone marked on the diagram; and, furthermore, application of TiO_2 or rutile (by brush) was enough to produce titanium Chun blues in many of the transparent zinc glazes, irrespective of alumina/silica values.

3. Addition of Opacifiers

Some glazes that would other wise be transparent will produce a Chun-blue with the addition of an appropriate opacifier. For example, P_2O_5 from bone ash or wood ash or other sources; TiO_2 (5% to 10%) from the pure oxide or rutile, such as the example mentioned above referring to the Zinc Set.

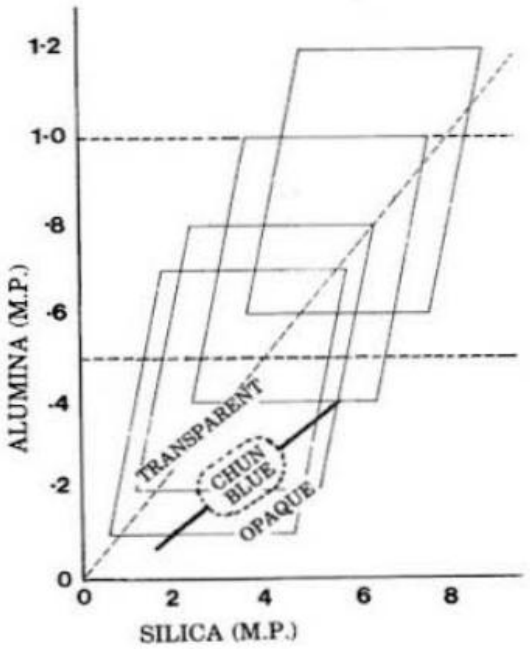
Note: Phosphorous pentoxide (P_2O_5) is an important opacifier in traditional Chinese glazes. It causes glass-in-glass colloid, and also bubble opacity, these phenomena being important in traditional Chun and celadon glazes. See the texts by Nigel Wood and Robert Tichane (References 9 and 10).

4. Addition of Iron Oxide

Iron oxide often plays an important part in the production of Chun blues. Sometimes it is added to the glaze, but traditionally it

DIAGRAM 18.2

Under favourable conditions, the Chun-Blue effect will occur where indicated, in the Zinc Set, the 0.8 and 0.9 Limestone Sets and the Magnesium Set.



is present in the body or in an iron-rich slip beneath the glaze. Sometimes the Chun glaze is put over a tenmoku-type glaze. The role of the iron seems to be partly optical (to absorb the red wavelengths, as mentioned before) and partly chemical. The chemical role is a little obscure, but Hamer (Ref. No.2, page 164) mentions that in reduced glazes:

> '... low alumina content, almost amounting to absence, encourages a blue in part saturation (of the iron oxide). The presence of phosphorous pentoxide (P_2O_5) as a glass former also encourages the blue.'

It may be, of course, that the blue from the iron is a solution blue, and not an optical blue (called here 'Chun-blue'). You will find in some of the more startling blues of Chun-type glazes that the potter has used solution blue from cobalt (and iron?) to reinforce the overall blue effect. Hamer also mentions in regard to reduction and Chun glazes (page 56):

> '... It is essential to incorporate the iron oxide in ferrous silicate nuclei which remain separate from the surrounding glass.'

So it seems it may play an important role (under reduction) in the formation of crystal nuclei that are responsible for the Chun-blue.

A third possible role for iron is simply as a flux (in reduction) providing the small added degree of maturity necessary to produce Chun-blue in what would otherwise have been merely an opaque glaze. If this applies, the glaze will produce the effect without the iron if fired a little higher, though the colour will not be as deep.

Note: 'Solution' colour occurs when a colourant dissolves in a liquid to give a coloured liquid.

5. Firing Conditions

The importance of reduction has already been mentioned. (This does not apply to zinc glazes of course.)

One of the main types of opacifying agents is crystal nuclei, or minute crystals; therefore, factors bearing on formation and growth of these will bear on the achievement of Chun-blue (and opaque) glazes. (See 'Important Factors in Crystal Growth' in Chapter 16.)

If all other factors are favourable for formation of a Chun-blue glaze, temperature will affect the result in the following way:

Underfiring will give an opaque glaze, correct maturing will, of course, give the Chun-blue, and overfiring will produce a transparent glaze:

INCREASING TEMPERATURE →

OPAQUE... CHUN-BLUE... TRANSPARENT

So variation of the maturing temperature is one way of 'crossing the threshold'.

6. Glaze Thickness

Varying glaze thickness is another way of 'crossing the threshold'. You will often find different areas on the same pot showing transparent areas, Chun-blue areas and opaque areas, according to the glaze thickness. The transparent areas appear where the glaze is too thin, the opaque areas where it is too thick to produce the Chun-blue:

DECREASING THICKNESS →

OPAQUE... CHUN-BLUE... TRANSPARENT

The reason for the transparent glaze where thin is probably that:

(i) the glaze is richer in alumina near the clay/glaze interface and
(ii) Hamer suggests that it is simply that insufficient blue light is scattered (Reference No.2, page 56).

SUMMARY OF MAIN FACTORS AFFECTING CHUN-BLUE

a. Use glazes low in alumina and silica, with the alumina/silica ratio at 1:12 approximately.
b. Apply the glaze very thickly, especially in first trials.
c. Apply the glaze over an iron-rich slip or body, or over a tenmoku-type glaze.
d. Add iron oxide to the glaze, e.g. 1%-2%.
e. High silica ash, e.g. grass ash, is a good way of introducing the silica.
f. P_2O_5 may be tried (from bone ash or wood ash). The usual content of P_2O_5 in traditional Chun glazes is 0.5% to 1.5% P_2O_5. (Reference No. 9 page 45) This would be obtainable from 1% to 3% approximately of bone ash, if the bone ash is pure $Ca_3(PO_4)_2$.
g. Fire under reduction. (This does not apply to zinc-Chun glazes.)
h. If preliminary results are opaque, fire higher; or if transparent, fire lower.

CHUN-TYPE GLAZE RECIPES

I prefer to keep the name 'Chun Glaze' for the traditional Chinese Chun glaze. Some of this type are listed here. However, I have also included some glazes that I would hesitate to call 'Chun Glazes', though they do develop the optical blue, or what I have called Chun-blue effect.
Note: 'A:S' equals 'alumina/silica ratio'.

a. TICHANE (Ref.10, page 74)

Recipe (Tichane):	
Potash Feldspar	48
Silica	31
Limestone	20
Bone Ash	1
Magnetite	1

SEGER FORMULA		OXIDE WEIGHT %	
0.3 K_2O 0.7 CaO	0.3 Al_2O_3 3.61 SiO_2 Plus 1% Bone Ash and 1% Fe_3O_4 (A:S...1 : 12)	K_2O CaO Al_2O_3 SiO_2	10.2 14.1 11.0 77.9
		Plus 1% Bone Ash and 1% Fe_3O_4	

b. SUNG CHUN (Taken from *Sung Sherds* by Sundius, and given in Tichane, page 74, and also Wood, Ref. 9, page 45).

Chemical Analysis OXIDE	WT% (Sundius)
SiO_2	72.79%
Al_2O_3	9.94
Fe_2O_3	1.58
TiO_2	0.07
MgO_2	1.50
CaO	8.80
Na_2O	0.72
K_2O	3.85
P_2O_5	0.54

SEGER FORMULA		RECIPE	
0.22 KNaO 0.64 CaO 0.15 MgO	0.4 Al_2O_3 4.9 SiO_2 Plus 1.58% Fe_2O_3 and 0.5% P_2O_5 (A:S...1 : 12.5)	K-FELDSPAR WHITING TALC KAOLIN SILICA	28.3 14.8 4.4 10.7 41.9
		Plus 1.58% Fe_2O_3 and 0.5% P_2O_5	

(The 0.07 TiO_2 is probably undesirable but also unavoidable as an impurity in glaze ingredients.)

c. CARDEW (Ref.7, page 142)
Cardew's recipe refers to some materials unavailable here, so I will let you work out your own recipe. Cardew recommends talc as the source of MgO.

0.34 KNaO 0.47 CaO 0.19 MgO	0.357 Al_2O_3 3.54 SiO_2 Plus 1.8 Fe_2O_3 and 0.7 P_2O_5.

d. LEACH (Ref.6, page 165)
According to Leach:
'Hamada gives a proportion of limestone 1, quarts 2, and feldspar 3, as a sound basis for experiments.'
However, he is talking about 'celadon' glazes, not Chuns! But if you take this glaze, and add, say, 1% Fe_2O_3 in the hope of getting a Celadon you will most likely end up with a Chun-blue glaze, which does not differ much from, say, glaze (a) (from Tichane):

RECIPE (Leach)	
WHITING	16.7
SILICA	33.3
FELDSPAR	50.0
RED IRON OXIDE	1.0%

SEGER FORMULA	OXIDE	WT%
0.33 KNaO 0.33 Al_2O_3 4.0 SiO_2	K_2O	9.1
0.66 CaO Plus, say, 1% Fe_2O_3	CaO	10.0
	Al_2O_3	9.8
(A:S...1 : 12)	SiO_2	71.1
	Fe_2O_3	1%

This is an illustration of the fact that there is no sharp dividing line between Chuns and celadons.
Leach also gives the following recipes on page 173:

Chun or Yuan:	1.	2.	3.
Feldspar	58	55	30
Medium Ash	21	15	40
Reed Ash	16	25	30
Limestone	5	5	—

e. Some of the glazes in the Celadon Experiment C(i) (see later) give excellent Chun glazes. For example, Glaze C16 with 1% iron oxide and 1% bone ash should give a good Chun glaze if applied over an iron-y slip or body, and fired in reduction to the appropriate temperature (around 1300°C).

REFERENCES:

1. *Glazes for the Craft Potter* by Harry Fraser (Pitman).
2. *The Potter's Dictionary of Materials and Techniques* by Frank Hamer (Watson/Guptill).
3. *Ceramic Glazes* by Cullen Parmelee (Cahners Books).
4. *Industrial Ceramics* by Felix Singer & Sonya S. Singer (Chapman and Hall).
5. *Fundamentals of Glazes* (in Japanese) by Kado.
6. *A Potter's Book* by Bernard Leach (Faber and Faber).
7. *Pioneer Pottery* by Michael Cardew (Longman Cheshire).
8. 'Chun Glazes' in *Pottery in Australia*, 7/1 Michael Cardew.
9. *Oriental Glazes* by Nigel Wood (Pitman).
10. *Those Celadon Blues* by Robert Tichane (The New York Institute for Glaze Research).
11. *Glazes for Australian Potters* by Janet DeBoos (Methuen).

19 DECORATED WHITEWARE GLAZE FIT

The production of white pottery has been a perennial preoccupation with potters, going back over a thousand years. The Tsu Chou and Ching Pai (Ying Ching) of China, the Shino of Japan, the Maiolica and Delft of Europe are all expressions of this desire. Once obtained, the white pottery usually has become the background for decoration; and while one can be critical of styles where the pot has been lost as it became mere surface for decoration, it is nevertheless possible for a sensitive approach to achieve an integration of decoration and form. These aesthetic considerations, however, are outside the scope of this course: the object of this Chapter is to give you the techniques to enable you to develop your own style of white pottery with coloured decoration. I would suggest you follow this procedure:

Developing Whiteware with Coloured Decoration:

1. Decide whether the whiteness is to come from the body, a slip or an opaque white glaze or a combination of these.
2. Decide on the body to be used. If necessary, develop the body.
3. Develop a white slip (if applicable).
4. Develop a palette of colours from pigments and/or slips and/or engobes.
5. Develop suitable glazes.

Each of these steps will now be discussed in turn.

WHITENESS — HOW WILL YOU GET IT?

Table 19.1 shows three broad approaches.

For extra whiteness you may want to combine two of these approaches (though it should not really be necessary), e.g. high quality industrial porcelain will often use a combination of a white body plus a white opaque glaze. Going in the other direction, if you use a dark body with semi-opaque slip or glaze, variations in thickness of the slip or glaze will give beautiful and subtle changes in tone as the dark body is alternately concealed or half revealed.

BODY

You may wish to use your normal stoneware body and rely on a white slip or opaque white glaze for the white result. This way you can use a clay with good working properties and avoid the problems, such as reduced plasticity, that are usually associated with a very white body.

TABLE 19.1

White Pottery		Suitable Coloured Decoration
a. White body, e.g. porcelain or white stoneware with a suitable 'clear' glaze.	+	Coloured slips under the glaze and/or coloured pigments under or over the glaze.
b. White slip over the body (which is usually darker) with a suitable 'clear' glaze.	+	Same as above.
c. White opaque glaze over any body	+	Coloured pigments over the opaque glaze.

A good quality porcelain, however, will give a finished result not achievable by lesser materials. White stonewares, such as Walker's No.10, and porcelains, such as Podmore's porcelain, are readily available, though sometimes expensive. If you wish to develop your own stoneware or porcelain, see McMeekin's book (Ref. No.1.)

WHITE SLIP

(*Note*: The development of coloured slips and engobes will also be touched on here although they relate to step No.4.)

1. Requirements of Slips

a. The slip must smooth out the roughness of the body (if this is desired), be adequately opaque and white (if this is desired) or provide some desired colour.
b. It must cling in shrinking and firing and not crack or fall off due to differential shrinkage. However, cracking is sometimes desired as a textural surface effect.
c. It must fire hard enough or vitrify enough for the purpose.
d. It must survive under the glaze without running or peeling or checking etc.

2. Composition of Slips

When dealing with slips, engobes and pigments, you will find that percentage figures are nowhere near as critical as with glazes — one can be far more casual with these recipes than with glaze recipes.

Note that the terms *slip* and *engobe* are virtually interchangable, though the word *slip* implies that clay is present, usually as a major ingredient, whereas some *engobes* contain no clay at all.

Two approaches will be dealt with: a) using body clay as the basis of the slip and b) fully compounding the slip from basic ingredients.

a. Using Body Clay

A common approach is to use one of your normal clay bodies as the slip if shrinkage and colour/tone factors are compatible. For example, slip made from Walker's No.10 white stoneware body has been used as an off-white slip over darker stoneware. Also this would be a good base for adding colouring oxides for coloured slips, as long as the slip/body shrinkages are compatible. (More on shrinkages below.) Sometimes if a slip is required that is darker than the body, the slip may be made from 100% of the same body plus the colourant. Such a slip may be sieved through a 60-100-mesh sieve to remove coarser particles, and it would need to be applied as early as possible, i.e. before the pot stiffens up too much.

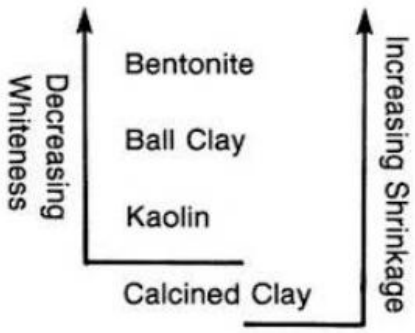
b. Compounding the Slip

By compounding the slip from basic ingredients such as feldspar, silica, ball clay etc., it is relatively easy to manufacture a slip with just the properties that you require; shrinkage can be adjusted to give optimum results, whiteness of colour can be achieved etc.

There is a good discussion of this approach in Daniel Rhodes' *Clay and Glazes for the Potter*, Chapter 26, 'Engobes'. The following is a summary from this and other sources:

(i) Clays

The types of clays used in a slip are chosen mainly for their whiteness (or colour) and their shrinkage. Other factors such as fineness, stickiness etc. may also be of importance, though these factors tend to be tied in to shrinkage and colour to a certain degree. The following is a useful generalisation with regard to shrinkage and whiteness, but like any generalisation in ceramics, there are exceptions:



One can usually make do with ball clay and kaolin, though bentonite can be used if a high shrinkage is required without too high a clay content; and calcined clay is commonly used to reduce shrinkage when, for example, applying slip to bisque ware. Some ball clays are whiter than others, and this should be taken into account if compounding a slip where whiteness is to be maximised. For example, ball clay 'C' fires whiter that ball clay 'QA'.

A low clay content in the slip may be accompanied by crazing.

(ii) **Fluxes**

Feldspar is the most common flux in stoneware slips. Commonly around 20% is used, higher for a vitreous slip, but this may be accompanied by crazing. Also, higher vitrification may allow the colour of the body to appear or allow the slip to react with iron oxides in the body.

Whiting is rarely used but may be important. 1% to 2% can have a powerful fluxing effect in the presence of feldspar, thereby reducing the amount of feldspar needed.

(iii) **Fillers**

The main filler used (non-plastic, refractory) is silica. It lessens shrinkage, increases hardness, improves whiteness and, according to Rhodes, improves glaze fit.

(iv) **Hardeners**

These are used to improve the green strength of the slip and promote adhesion to the body. In many cases this function will be performed by ball clay or bentonite (or any plastic clay), but other hardeners may be used, such as borax, or organic binders (e.g. gum tragacanth) or a glue like Aquadhere. Slips with gums and glues in them should be used when fairly fresh.

(v) **Opacifiers**

These are not necessary for darker slips. Usually an opacifier grade of zircon would be used for a white slip.

(vi) **Colourants**

See under Coloured Slips and Engobes.

3. **Recipes for Compounded Slips**

See data box on this page for several recipes for stoneware slips taken from Rhodes.

4. **Trouble Shooting**

Many of the problems associated with slip will be resolved by consideration of the previous discussion. For those new to slips, I will detail a couple of the most common problems that occur during application to raw ware. These problems are also met with in 'raw glazing' or 'slip glazing'.

a. If the slip lifts off or falls off, especially before the firing, this will probably be due to the pot shrinking more than the slip as they dry. You can overcome this by adjusting the slip to have more drying shrinkage (see above), or by applying the slip more thinly, or applying it later (to a drier pot). If the slip cracks in drying, this is the reverse effect of the above. The slip is shrinking more than the body. This may be overcome by adjusting the slip to have *less* shrinkage, or (again) by applying the slip more thinly, or by applying it earlier (to a wetter pot). This problem may also be due to excess gum or glue.

b When applying slips to a raw pot, the pot may collapse or crack. If it collapses, the slip is being applied too early. If it cracks but maintains its form, the slip is being applied too late — it is common, however, to apply slip or slip glazes to bone dry pots if the clay body is fairly open.

Parmelee (Ref. No.3, page 402) has a comprehensive section on defects in slips and engobes, referring specifically to industrial practice; the principles, however, apply to our kind of work as well, and the section is well worth reading if you are having problems.

Read also the text by Fraser, page 72 on engobes.

	Damp pot	Dry Pot	Bisqued Pot
Kaolin	25	15	5
Ball Clay	25	15	15
*Calcined Kaolin		20	20
Leadless Frit			5
Nepheline Syenite			5
Feldspar	20	20	20
Silica	20	20	20
Zircopax	5	5	5
Borax	5	5	5

* Note: You can calcine your own kaolin by bisque firing some in, say, a cracked bisqued pot.

COLOURS

1. Coloured Slips and Engobes

Using a white slip as a base, addition of colouring oxides will produce coloured slips. The data box shows suggested percentage additions by two authors.

Some colours that are difficult to obtain from colouring oxides may be obtainable from commercial body stains or glaze stains. These will often require oxidation fire, and you should make sure that the colour is stable at stoneware temperature.

2. Colouring Oxides and Pigments

There is no sharp line between pigments, slips and engobes. The term *pigment*, however, is usually used if it is made up of predominately colouring oxide (or carbonate). Some of the 'pigments' I will list later are technically *slips*, but this is irrelevant; they are listed together because they are used together in the same way.

In general you will find that as with slips, percentages quoted for pigments recipes are not critical; large deviations are possible in the amounts and types of ingredients.

It is well worth reading Leach and Cardew on pigments. See Ref. No.5, (Leach) Chapter 6, pages 127-130, and Ref. No.6, (Cardew), pages 149-150.

Most pigments can be applied over or under the glaze, though Leach suggests some flux (e.g. 25% feldspar or glaze) be added to a pigment used *over* the glaze to avoid it being too metallic. If you want to practise your brushwork on your pots, I recommend you use pigments (or slips) applied *under* the glaze — it is relatively easy to wash the pigment (or slip) off the pot if you make a mistake and have another go before applying the glaze. Gwynn Pigott suggests that if the glaze being used contains no clay (and is therefore powdery) one should decorate before applying the glaze.

The reason we rarely use pure colouring oxides or carbonates as pigments is that most are very strong colourants and need a little thinning down to make them easier to use without producing a metalic overload. Iron oxide is often used without addition, but even here, it is common to add 20% to 50% of clay to suspend it and improve its flow from the brush.

Talc is sometimes added (e.g. 10%) to aid flow from the brush.

Australia is particularly rich in minerals that can be ground up and used as pigments. A geologist should be able to help you find local rocks and minerals containing colouring oxides such as iron, copper, manganese, nickel, cobalt etc. It is most unlikely, of course, that you will find all these in one locality, but if you enquire of

From Rhodes

Oxide Additon	Colour
2% — 15% Iron oxide	gives a range of earthy colours from tan to brown to metallic
1% cobalt oxide	blue
1% cobalt oxide 2% iron oxide	grey-blue
10% vanadium stain	yellow
6% manganese oxide	purple-brown
3% iron oxide 2% cobalt oxide 2% manganese oxide	black
and others.	

From Parmelee

Oxide Additon	Colour
2% — 10% cobalt oxide	blue (light to dark)
5% — 10% chrome oxide	green (light to dark)
2% — 10% nickel oxide	grey/grey-green/loam
and others.	

potters, rock and gem collectors, and geologists as you travel around the country, you will gradually build up a collection of pigment sources (and other minerals, such as feldspar, kaolin etc.); in most cases, once you have found a source, you have got it for life, just for the trouble of digging it out and grinding it up when you need it. With pigments (as opposed to feldspar, kaolin etc.) you can often get a lifetime supply in one visit. You can test unidentified rocks for their usefulness as pigments by pulverising a small amount with a hammer and firing a little of the powder on a tile under a clear limestone glaze.

Most colouring oxides are active fluxes, and a heavy application of the pure oxide over or under the glaze will often make it run. The clay content in a pigment can help prevent this. The more the colouring oxide fluxes the glaze, the more the colour will diffuse into the surrounding area, giving a soft edge to lines, brushstrokes etc., and in the extreme, wash away with the runny glaze. Some colourants, such as industrial stains, chrome oxide, etc., are very stable and tend not to combine with the glaze. The colour is, therefore, unchanged by the firing; it stays where it is put and is opaque.

Impure and unrefined materials will often give more interesting results than the highly refined material that is usually bought off the shelf. A coarsely ground pigment can give interesting textural effects from flecking. 'Impurities' can 'soften' an otherwise harsh colour, either naturally (if using a natural pigment) or artifically (e.g. by adding iron, manganese, nickel oxides to a cobalt blue pigment).

Copper oxide is very useful in reduction for the production of reds, but there are problems associated with its volatility; if the end of the firing is unduly extended, you may find all your copper oxide has disappeared (up the chimney) leaving an unmarked glaze. I use a copper pigment that contains an iron-bearing clay that leaves a trace of the brushstroke even if all the copper vaporises. Also, I would avoid use of this pigment in, say, a Shino firing, where the end of the firing is quite extended.

3. **Pigment Recipes**

(i) *Kawai pigments* — Summarised from a number of sources, including Bernard Leach, Doug Lawrie and Shigeo Shiga.

Blue:	Fine red clay	75	Red:	Black copper oxide	60
	Amakusa*	25		Zinc oxide	28
	Cobalt oxide	1.2%		Tin oxide	3
	Red iron oxide	1.7%		Hard carboniferous ash**	9

Notes:

* Amakusa is a standard glaze ingredient in Japan, similar to Cornish stone but with less fluxes. In this case you could use Cornish stone; I use dried raw porcelain body scraps.

** Hard carboniferous ash here refers to rice straw ash or other grass straw ashes. It assists in obtaining local reduction. Leach points out that fine (200 mesh?) carborundum (silicon carbide) would do a better job. It is available from abrasives manufacturers and pottery supply shops.

Other Kawai pigments:

50/50 clay and iron oxide, for Tessha, and iron colours. 50/50 iron oxide and rutile, for crystalline yellow. Mix of cobalt, copper and iron, for black.

Kanjiro Kawai was a friend of Leach's, and developed a style of pottery using trailed slip and underglaze pigments that has influenced handmade pottery around the world. These pigments would usually be applied by brush on bisque ware under a clear limestone glaze.

(ii) *Cardew pigments* — See Ref No.6, page 149. Cardew's pigments are meant to be applied on top of the glaze.

Iron Pigment:		Subdued blue:		Green: (for Orton Cn 9, Reduction)	
Fe_2O_3, or Fe_3O_4	80%	Cobalt carb.	20%	Chrome oxide	20%
Clay	20%	Tin oxide	20%	Plastic clay	10%
		Manganese oxide	10%	K Feldspar	30%
		Talc	10%	Silica	20%
		Plastic red clay	15%	Fluorspar	20%
		China clay	20%		
		Red iron oxide	5%		

Leach (page 130) and Cardew (page 149) give similar recipes for artificial Gosu, which is the mineral asbolite, used by the Chinese potters for their cobalt blues. The following from Cardew:

Artifical Gosu:	Cobalt oxide	20
	Manganese dioxide	40
	Iron oxide	30
	Plastic red clay	10

(iii) *Rhodes pigments* — See Ref. No.2, page 166.

Brown:		Black:	
Iron oxide	30 parts	Red iron oxide	10 parts
Chrome oxide	28 parts	Chrome oxide	76 parts
Zinc oxide	72 parts	Cobalt oxide	20 parts
		Manganese dioxide	12 parts
Blue:			
Cobalt oxide	26 parts		
Zinc oxide	104 parts		
Silica	70 parts		

Pure Oxides as Pigments

If you have worked through the exercises in Part I, you will have considerable experience in using pure colouring oxides as pigments. You should also have some idea of the limitations of this technique with regard to overloading or underapplying some oxides. If applying the oxides under the glaze, it is advisable to add a little glue or ball clay to the oxide to prevent the glaze from crawling off the decoration.

GLAZES

1. Transparent Glazes

If using a white body or slip, you will probably use a transparent glaze or possibly a semi-opaque glaze. This will allow you to use both under- and over-glaze pigments and under-glaze coloured slips. See Table 19.1, types (a) and (b). A study of your fired sets of base glazes from Part I (or if you have not done this, a study of the Results Charts will help) should give a good guide as to suitable transparent and semi-opaque glazes. The high Limestone Sets and Barium Set should both provide some useful starting points. To eliminate crazing, consider the Magnesium Set (and in oxidation, the Zinc Set as well). Perhaps blend a little magnesium and/or zinc into a limestone or barium glaze to eliminate crazing without losing transparency. And of course give good consideration to alumina and silica proportions (see Diagram 19.1).

Glazes towards Corner B will tend to be uncrazed and stiff (i.e. not runny), and pigments will tend to stay put. If glaze fit is properly adjusted, the pottery will be very strong. This kind of glaze is used by many professional potters for functional dinnerware.

Glazes towards Corner C will tend to be crazed, and if crystals do not form in the cooling, shinier than around B; and pigment will tend to run (which can be controlled in a pleasant way, but which can be disastrous without precise kiln control). These glazes being lower in silica will tend to be softer, more easily scratched.

2. Opaque Glazes

If using an opaque glaze, you can use any of the approaches to making shiny white opaque glazes mentioned in Chapter 18, or alternatively you could use a matt opaque glaze such as those produced in the Magnesium Set (usually around 0.3 Al_2O_3, 3.5 SiO_2, but depending on firing temperature), or a matt glaze that you have added an opacifier to (to make it fully opaque).

GLAZE FIT

... How to eliminate (or produce) crazing without changing the general character of the glaze.

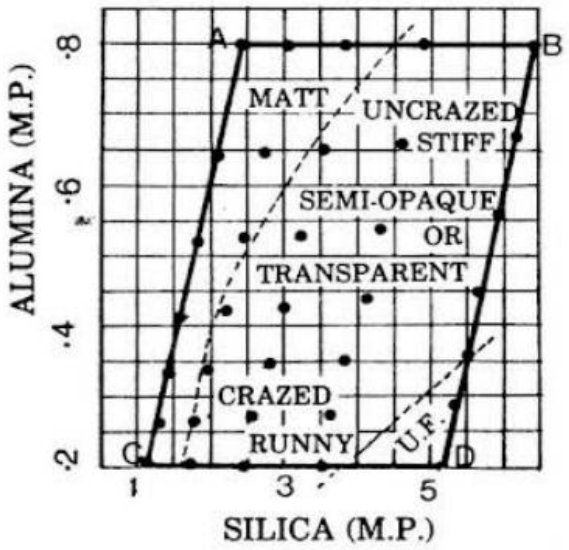
The usual discussion of glaze fit I will not cover here since it is well dealt with in many pottery texts. For example, see the text by Fraser (Ref. No.4) pages 106 to 110, 'Crazing' and 'Peeling'. I will confine myself here to the problem of reducing crazing without otherwise changing the character of the glaze. (To promote crazing, the recommendations are applied in reverse.)

To eliminate extreme crazing in a glaze without changing any other glaze features may be impossible, but one is rarely in this extreme position.

The following are a number of steps you should try individually or in combination to eliminate or reduce crazing:

(a) **Increase alumina and silica** but maintain the same Al_2O_3/SiO_2 ratio. This is what is happening in Diagram 1 as you go from corner C to corner B; in this case we can make large increases in alumina and silica (both of which will reduce the coefficient of expansion of the glaze) and

DIAGRAM 19.1
Effect of Alumina and Silica on Crazing and Glaze Maturity



eliminate crazing while maintaining the transparent nature of the glaze.

(b) **Fluxes**
See Hamer (Ref. No.7) page 147, and also page 336 for comprehensive tables showing relative thermal expansion and contraction rates. Table 19.2 shows the table from page 147.

Consider the fluxes in two groups: R_2O, and RO. By a study of Table 19.2, you should be able to see that, for example, replacing Na_2O by Li_2O, molecule for molecule, should reduce crazing. By this I mean you could replace, say, 0.2 M.P. of Na_2O by 0.2 M.P. of Li_2O. Consider next the RO fluxes, and it will be seen that MgO or ZnO could be used to replace some CaO, or BaO, in the glaze. Compare your limestone, barium, magnesia and zinc base glaze sets for the relative extent of crazing. See also the crazing diagrams in Chapter 7 (Diagram 7.2).

(c) **Adjust the body.** Some glazes need a very specific base glaze for the desired effect to appear. In this case, adjustment to the body may be the best solution. It may be a simple matter to use a different body that you already have available, or you may have to compound one specially for the job. Simple addition of 200-mesh silica (add to the slipped clay) will reduce crazing by increasing production of cristobalite. It will also make the body more porous. Addition of grog will usually tend to *increase* crazing.

(d) **Adjust the firing.** Bear in mind that the three common forms of silica may be present in the clay:

(i) Cristobalite with high thermal expansion and contraction.
(ii) Quartz with medium thermal expansion and contraction.
(iii) Silica glass with a very low thermal expansion and contraction.

Before the firing, the silica is mostly present as quartz. This is slowly converted to cristobalite at stoneware temperatures in an irreversible change, so multiple firings of the same pot will produce more cristobalite. This will cause large thermal expansion. It is possible, however, for over-vitrification to change this by converting the cristobalite to melted silica glass, with a very *low* thermal expansion.

So... an underfired pot may craze because of insufficient cristobalite formed in the body. In the production of vitreous porcelain, however, overfiring may cause crazing by converting too much of the cristobalite to glass.

REFERENCES:

1. *Notes for Potters in Australia* by Ivan McMeekin (NSW University Press).
2. *Clay and Glazes for the Potter* by Daniel Rhodes (Pitman).
3. *Ceramic Glazes* by Cullen Parmelee (Cahners Books).
4. *Glazes for the Craft Potter* by Harry Fraser (Pitman).
5. *A Potter's Book* by Bernard Leach (Faber and Faber).
6. *Pioneer Pottery* by Michael Cardew (Longman Cheshire).
7. The Potter's Dictionary of Materials and Techniques by Frank Hamer (Watson/Guptill).

TABLE 19.2
Relative Thermal Expansion and Contraction of Oxides in Glazes

Fluxes	Amphoteric and Acidic Oxides	Crystallisers and Opacifiers
Na_2O		
K_2O		
CaO		CaO
BaO		BaO
PbO		
		TiO_2
Li_2O		
ZnO		ZnO
MgO		MgO
		ZrO_2
		SnO_2
	Al_2O_3	
	SiO_2	
B_2O_3	B_2O_3	

Increasing Rate of Expansion

20 HIGH IRON GLAZES

Iron glazes are a tremendous challenge to the stoneware potter; and after centuries of use, like any real challenge, they continue to fascinate and inspire. Part of the challenge arises from there being so many factors interrelated to give the final result; and herein lies my greatest problem, in trying to understand for myself and explain the picture to you. The reason we bother is that the rewards can be considerable, at the possible expense of feeling rather humbled as we fail again and again to obtain the kind of quality that came very easily (so it seems) to Chinese potters a thousand years ago.

I will consider iron glazes in two parts: high iron glazes, as typified by tenmoku, and low iron glazes, as typified by celadon. The two overlap, but it is a convenient division for our purposes.

HIGH IRON GLAZES

Definitions

Honey Glaze — A transparent brown or amber or yellow glaze, the colour depending to a large extent on the colour of the body which is visible under the glaze. This colour is caused by the same form of iron oxide that gives the brown colour in beer bottle glass.

Tenmoku — A black iron glaze, usually shiny, and often breaking to rust where thin.

Kaki — A rust coloured iron glaze — the iron oxide crystals are not visible to the naked eye. The name is Japanese for 'persimmon'.

Tessha — There seem to be two definitions in popular use. In Hamer's *Dictionary* it is defined as 'A variation of the tenmoku glaze in which the rust parts spread in patches over about half the surface', i.e. a stage halfway between 'tenmoku' and 'kaki'. The literal translation of the Japanese word *tessha* is 'iron sand', which refers to spangles of hematite (Fe_2O_3) that are visible to the naked eye. These visible crystals seem to be essential to the Japanese definition -- the glaze colour may be from a reddish-brown to a dark purple. This is the definition I will use. In the diagrams following, the zones marked '50/50 black rust' correspond to Hamer's 'tessha'.

Teadust (Called 'soba' by the Japanese) — An iron glaze containing green or yellow-green proxene crystals in spots or covering the entire surface.

Forms of Iron Oxide in Glazes

Iron oxide may exist in glazes in several forms:

a. as a part of the glass network, replacing silicon in the silica chains. In this form the iron is colourless.
b. in the oxidised form, Fe_2O_3, producing kaki, rust, honey etc.
c. in the reduced form, FeO, producing blues and blue green
d. in the neutral form, Fe_3O_4, which is a combination of forms b. and c. giving black (grey in thin section).

Most, if not all, iron glazes contain a mixture of all the different forms of iron listed above.

For more depth in this theory, I recommend you read Reference 4 by Hughan, and Reference 3 by Hamer.

Unity Formula Convention for Iron Glazes

As you know, the normal convention when calculating a glaze formula is to bring the fluxes to unity. Reduced iron oxide acts as a flux, and theoretically one should include the iron oxide in the RO (fluxes) column as FeO if the glaze is meant to be fired in reduction. I will not do this here since the sets of tests are meant to be fired under varying degrees of oxidation/reduction, and it becomes a difficult and probably pointless exercise to try to allow for iron oxide that is acting as a flux, merely to be able to uphold the unity formula convention. So all the glazes in the experiments listed will have the base glaze calculated to a unity formula, and the iron oxide added as a 'percentage' on top of '100%' of the base glaze.

EXPERIMENTS

The following seven experiments give a good cross section of high iron glazes.

EXPERIMENTS Fe1, Fe2 and Fe3

Three sets of fluxes are used, and alumina and silica varied.

The 'corner glazes' can be taken from the Data Sheet: Glaze A = Glaze No. 1; B = 4; C = 13; D = 16. Add 8% Red Iron Oxide to each corner base glaze.

There are 16 glazes in each experiment, each being represented on the Results Charts by a large dot.

Volumetric Parts Chart and Glaze Numbers for Experiements Fe1, Fe2 and Fe3

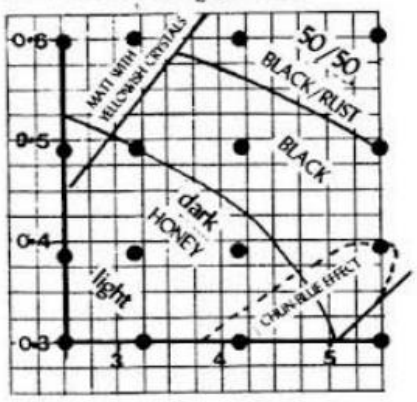
90 | 0 1 0 | 0	60 | 30 2 0 | 0	30 | 60 3 0 | 0	0 | 90 4 0 | 0
60 | 0 5 30 | 0	40 | 20 6 20 | 10	20 | 40 7 10 | 20	0 | 60 8 0 | 30
30 | 0 9 60 | 0	20 | 10 10 40 | 20	10 | 20 11 20 | 40	0 | 30 12 0 | 60
0 | 0 13 90 | 0	0 | 0 14 60 | 30	0 | 0 15 30 | 60	0 | 0 16 0 | 90

Firing and Clay Body

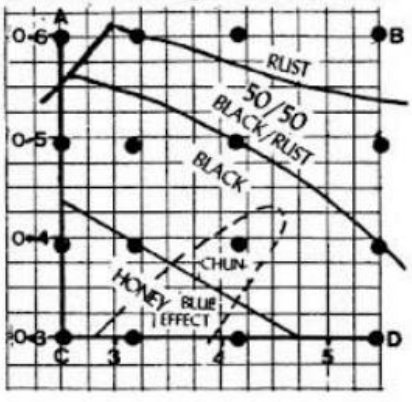
The glazes are meant to be fired in reduction to at least Orton Cone 10. Use a similar testing procedure to that outlined for the base glazes in Part I i.e. work with assessment tiles first, then apply interesting looking glazes to individual tiles. Use a range of clay bodies in the assessment tiles, including iron-y bodies. Results will vary considerably depending on firing and clay body.

RESULTS CHARTS

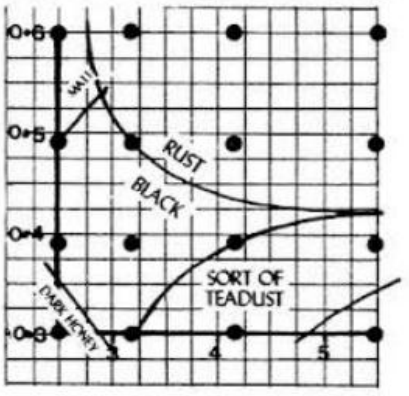
EXPT. Fe1 RO: 0.3$K_2$0, 0.7CaO



EXPT. Fe2 RO: 0.3$K_2$0, 0.55CaO, 0.15MgO



EXPT. Fe3 RO: 0.3 K_2O, 0.4CaO, 0.3 MgO



ALUMINA (M.P.)

SILICA (M.P.)

Data Sheet

Add 8% Red Iron Oxide to each recipe.

The Al_2O_3/SiO_2 M.P. figures for Experiments Fe2 and Fe3 are the same as for Experiment Fe1.

Experiment Fe1

GLAZE No.	RECIPES K-FEL-DSPAR	WHITING	KAOLIN	SILICA	M.P Al_2O_3/SiO_2
1	52.1	21.9	24.2	1.9	.6/2.5
2	45.8	19.3	21.3	13.7	.6/3.2
3	39.6	16.6	18.4	25.4	.6/4.2
4	33.3	14.0	15.5	37.2	.6/5.5
5	54.7	23.0	16.1	6.3	.49/2.5
6	47.9	20.1	14.2	17.8	.49/3.2
7	41.1	17.3	12.2	29.4	.49/4.2
8	34.3	14.4	10.3	40.9	.49/5.5
9	57.2	24.0	8.1	10.7	.39/2.5
10	49.9	21.0	7.1	22.0	.39/3.2
11	42.6	17.9	6.2	33.4	.39/4.2
12	35.3	14.9	5.2	44.7	.39/5.5
13	59.8	25.1	--	15.1	.3/2.5
14	52.0	21.8	--	26.2	.3/3.2
15	44.1	18.6	--	37.3	.3/4.1
16	36.3	15.3	--	48.4	.3/5.5

Experiment Fe2

GLAZE No.	RECIPES K-FEL-DSPAR	WHITING	MAG. CARB.	KAOLIN	SILICA
1	52.5	17.3	4.0	24.3	1.9
2	46.2	15.2	3.5	21.4	13.7
3	39.8	13.2	3.0	18.4	25.6
4	33.5	11.1	2.5	15.5	37.4
5	55.1	18.2	4.2	16.2	6.3
6	48.2	15.9	3.7	14.2	17.9
7	41.4	13.7	3.1	12.3	29.6
8	34.5	11.4	2.6	10.3	41.2
9	57.7	19.0	4.4	8.1	10.8
10	50.3	16.6	3.8	7.1	22.2
11	42.9	14.2	3.3	6.2	33.5
12	35.5	11.8	2.7	5.2	44.9
13	60.3	19.9	4.6	--	15.2
14	52.4	17.3	4.0	--	26.4
15	44.4	14.7	3.4	--	37.5
16	36.5	12.1	2.8	--	48.7

Experiment Fe3

GLAZE No.	RECIPES K-FEL-DSPAR	WHITING	MAG. CARB.	KAOLIN	SILICA
1	52.9	12.7	8.0	24.5	1.9
2	46.5	11.2	7.0	21.5	13.8
3	40.1	9.6	6.1	18.6	25.7
4	33.7	8.1	5.1	15.6	37.6
5	55.6	13.3	8.4	16.3	6.4
6	48.6	11.6	7.4	14.3	18.1
7	41.7	10.0	6.3	12.4	29.7
8	34.7	8.3	5.3	10.4	41.4
9	58.2	14.0	8.8	8.2	10.8
10	50.7	12.2	7.7	7.2	22.2
11	43.2	10.4	6.5	6.2	33.7
12	35.7	8.6	5.4	5.2	45.1
13	60.9	14.6	9.2	--	15.3
14	52.8	12.7	8.0	--	26.5
15	44.8	10.7	6.8	--	37.7
16	36.7	8.8	5.6	--	48.9

EXPERIMENT Fe4

A: 1.0 CaO 0.5 Al_2O_3 4SiO_2 + 8% Fe_2O_3

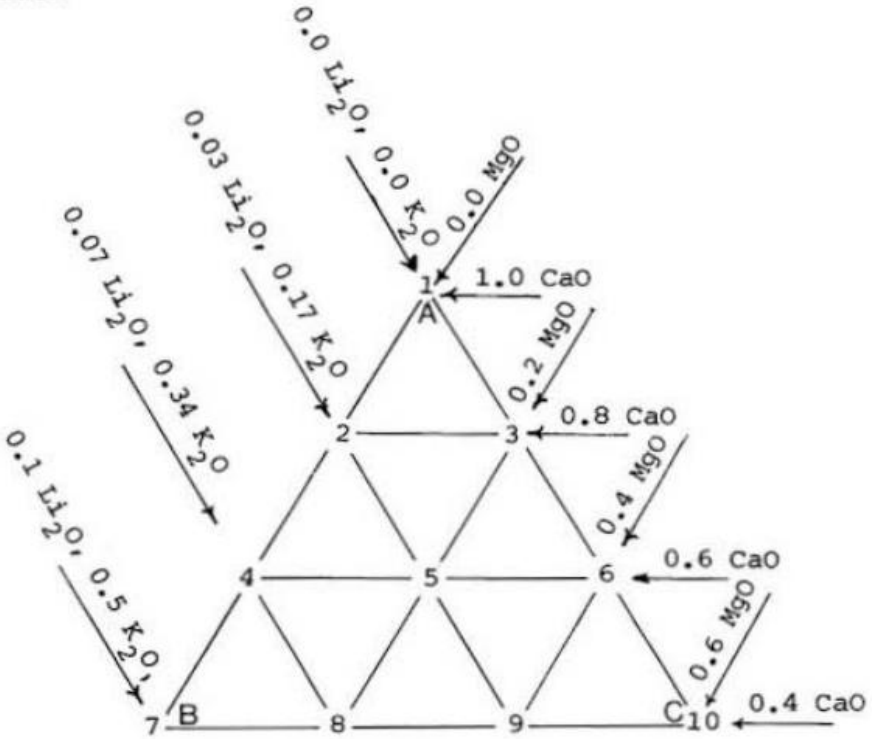
B: 0.5 K_2O
0.1 Li_2O 0.5 Al_2O_3 4SiO_2 + 8% Fe_2O_3
0.4 CaO

C: 0.4 CaO
0.6 MgO 0.5 Al_2O_3 4SiO_2 + 8% Fe_2O_3

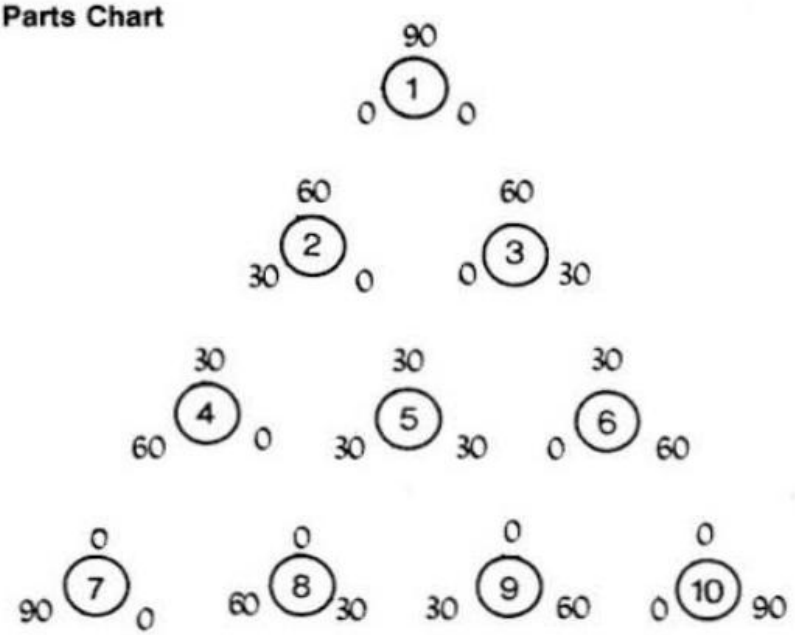
Alumina and silica are kept constant at 0.5 and 4.0 M.P. respectively, and fluxes are varied over a wide range to study the effect of CaO, MgO and R_2O-type fluxes in iron glazes.

The three 'corner glazes' can be taken from the Data Sheet: Glaze A = Glaze No. 1; B = 7; C = 10. Add 8% Red iron oxide to each corner base glaze.

Flux Variation



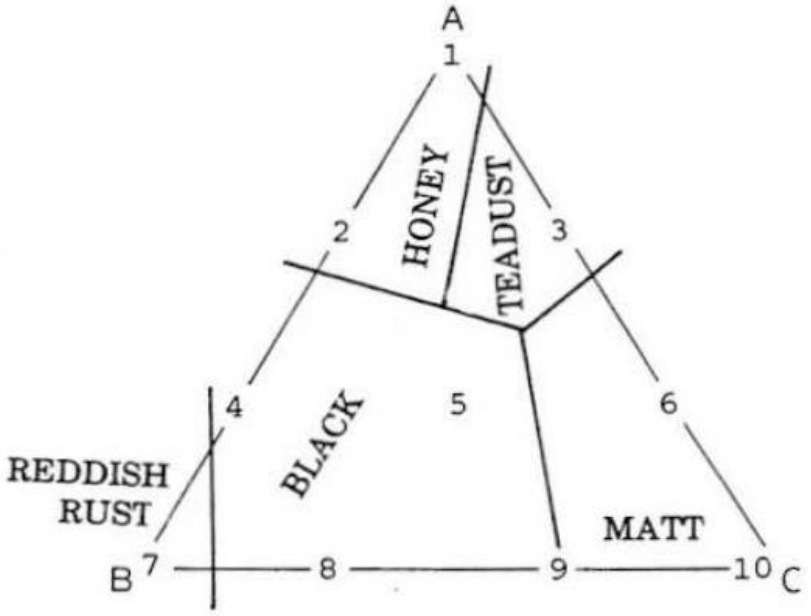
Volumetric Parts Chart



Firing and Clay Body:

Same as for Experiments Fe1, Fe2, and Fe3.

Results



Data Sheet

	RECIPES						SEGER FORMULAE					
GLAZE No.	LITHIUM CARB.	POTASH FELDSPAR	WHITING	MAG. CARB.	KAOLIN	SILICA	Li_2O	K_2O	CaO	MgO	Al_2O_3	SiO_2
1	--	--	24.5	--	31.5	44.0			1.0		.5	4
2	0.6	24.0	19.8	--	21.0	34.5	.03	.17	.79		.5	4
3	--	--	19.7	4.2	31.8	44.4			.8	.2	.5	4
4	1.3	48.1	15.1	--	10.5	25.1	.07	.34	.59		.5	4
5	0.6	24.0	15.0	4.2	21.3	34.9	.03	.17	.6	.2	.5	4
6	--	--	14.8	8.5	32.0	44.7			.59	.41	.5	4
7	1.9	72.1	10.4	--	--	15.6	.1	.5	.4	0	.5	4
8	1.2	48.1	10.3	4.2	10.8	25.4	.06	.34	.4	.2	.5	4
9	0.6	24.0	10.1	8.5	21.5	35.3	.03	.17	.4	.4	.5	4
10	--	--	10.0	12.7	32.3	45.1			.4	.6	.5	4

Add 8% Red Iron Oxide to each glaze

EXPERIMENT Fe5, Fe6 and Fe7

Each experiment is a line blend, starting with a base glaze, and adding progressive amounts of iron oxide up to 20%, by 2% increments.

Firing and Clay Body

Instructions here are the same as for Experiments Fe1, Fe2 and Fe3. Note that, if fired in reduction, those glazes with higher iron will be runnier because the iron acts as a flux.

Results

Experiments Fe5 and Fe6 produce celadon, then black, then rust as iron oxide is increased, the high alkali (R_2O) in Experiment Fe5 tending to produce the rust with less iron than Experiment Fe6.

Experiment Fe7 produces pyroxene crystals in all glazes, including some good teadust glazes.

Data Sheet

Fe5 SEGER FORMULA	OXIDE	WT%	RECIPES	
0.5 K_2O	K_2O	13.0	K-FELDSPAR	72.1
0.1 Li_2O 0.5 Al_2O_3 4 SiO_2	Li_2O	0.8	LITHIUM CARB.	1.9
0.4 CaO	CaO	6.2	WHITING	10.4
	Al_2O_3	14.0	KAOLIN	00.0
+0-20% Fe_2O_3	SiO_2	66.1	SILICA	15.6
	Fe_2O_3	+0-20%	RED IRON OXIDE	+0-20%

Fe6 SEGER FORMULA	OXIDE	WT%	RECIPES	
	K_2O	7.9	K-FELDSPAR	42.1
0.3 K_2O 0.5 Al_2O_3 4 SiO_2	CaO	10.9	WHITING	17.7
0.7 CaO	Al_2O_3	14.2	KAOLIN	13.0
	SiO_2	67.0	SILICA	27.3
+0-20% Fe_2O_3	Fe_2O_3	+0-20%	RED IRON OXIDE	+0-20%

Fe7 SEGER FORMULA	OXIDE	WT%	RECIPES	A	B	C
	K_2O	10.0	K-FELDSPAR	51.6	51.5	53.9
0.25 K_2O	CaO	10.7	MAG. CARB.	9.4	—	—
0.45 CaO 0.25 Al_2O_3 2.5 SiO_2	MgO	5.1	DOLOMITE	—	20.5	—
0.3 MgO	Al_2O_3	10.8	TALC	—	—	14.7
	SiO_2	63.5	WHITING	16.7	5.6	17.5
			SILICA	22.3	22.3	14.0
+ 0-20% Fe_2O_3	Fe_2O_3	+0-20%	RED IRON OXIDE	+0-20% each		

Discussion of Results

To a certain extent, the following phenomena act independently of each other and can, therefore, be considered separately.

1. Iron solubility
2. Rust break where glaze is thin
3. Chun-blue occurrence
4. Teadust crystals.

1. Iron Solubility — The series from honey to black to rust.

a. Varying Iron Oxide Content.

Let us look at what happens as we progressively add iron oxide to a base glaze: (See Experiments Fe5, Fe6 and Fe7).

(i) Smaller amounts of iron oxide in the glaze will be dissolved completely in either colourless or coloured form, typically producing a honey or celadon glaze.

(ii) If we add a little more iron oxide, the oxide is all dissolved during the firing, but as the glaze cools, some of it crystallises out to give results such as kaki, tessha etc. If the cooling is quick enough, the glaze becomes viscous before the crystals have time to grow, and the iron oxide remains in solution to give a typical shiny black tenmoku. (See Cardew page 140.)

(iii) If we continue adding iron oxide, a stage is reached where, even at top temperature, not all the iron oxide is dissolved, producing a dull matt opaque surface. Further additions of iron will produce a metallic overload effect.

This line blend addition of iron oxide gives the full range of iron solubility. However the series from 'honey to black to rust' (covered by (i) and (ii) above) can be produced in other ways, without varying the iron oxide content.

b. Varying Alumina and Silica

Examination of the Al_2O_3/SiO_2 charts will show that a steady increase in alumina and silica (keeping the Al_2O_3/SiO_2 ratio constantly at roughly 1:8) with iron oxide constant at 8% addition, the glazes go from honey to black to rust, just as was noted in the case of increasing iron oxide. For example, see Experiment Fe2.

Note that the high flux corner (C), favours honey, and the high alumina/high silica corner (B) favours the rust. Also it should be mentioned that this pattern is less obvious if the glaze is not matured enough, and if the cooling is too fast to allow proper crystallisation of the iron oxide. If slightly underfired, and quickly cooled, all the glazes from 'honey' to 'rust' can come out more or less black.

c. Lime/Alkali Balance (See Experiment No. Fe4)

The main alkali (i.e. R_2O) flux used in this case was K_2O from potash feldspar, but there was a little Na_2O from the same source and a little Li_2O (from lithium carbonate) as well. The line blend from corner A to corner B in Experiment Fe4 (i.e. from the lime corner to the alkali corner on the triaxial diagram) indicates that CaO favours honey or dark honey, and as the alkali is increased, the series passes through black to almost rust (red rust, with black where it is quite thick) at the R_2O end. So this experiment would indicate that lime favours solution of iron oxide, while alkali fluxes favour crystallisation. Comparison of the two line blends making up experiments Fe5 and Fe6 will also confirm this conclusion — in the high alkali line blend, the rust tends to appear with less iron oxide than is necessary in the lime series.

d. The Role of MgO

Substitution of MgO for some of the CaO seems to have three main effects:

(i) It causes the iron oxide to crystallise out more easily. A comparison of experiments Fe1 and Fe3 will show this.

(ii) It promotes the formation of pyroxene crystals, green or yellow green, especially in glazes low in alumina. See more under 'Teadust Crystals'.

(iii) In large amounts, it turns the glazes matt and brown.

e. The Role of BaO

Although it is not covered in the experiments, it is worth commenting here on the effect of BaO on iron solubility.

According to Kado (Ref. No. 6) BaO plays a similar role to CaO, favouring solution of the iron, rather than crystallisation.

The Role of the Colourless Iron

We have seen in (b), (c) and (d) above how we can get a glaze from a honey to a kaki in a series of glazes all containing, say, 8% addition of Fe_2O_3. It might seem that at the 'honey' end of the series, the iron is disappearing to somewhere. As far as I

know, it is impossible for significant amounts of iron to vaporise from this sort of glaze, so it is a reasonable assumption that the 'honey' glazes have more iron in the colourless form than the 'kaki'. In the case of (b) above, the production of honey in a high flux glaze is presumably the result of some of the iron standing in for silicon (in the silica chains) which is in short supply.

According to Hughan (Ref. 4) higher temperatures favour iron in the colourless form. Presumably longer soaking will have a similar effect.

2. 'Rust Break' Where Glaze Is Thin

Many high iron glazes, including tenmoku, teadust, some honey glazes etc. will break to rust where thin. The rust break is the clay/glaze interface which comes to the surface where the glaze is thin, and a period of reoxidation will usually turn it to an opaque rust or brown colour. The normal explanation given is that the glaze is richer in alumina in the clay/glaze interface, promoting the rust colour. However, visual observations we have made on rust break in tests varying alumina and silica seem to indicate the rust break zone is probably richer in both alumina *and* silica. Also, if the clay/glaze interface underneath, say, a thick tenmoku is exposed by grinding through to the body, no rust is evident. This indicates the role that reoxidation plays after the glaze has melted, most likely in the cooling process. For the same reason, rust break may be absent on draw trials taken at top temperature, but present on identical samples left in the kiln to cool slowly. This factor is important for people using rapid firing/cooling cycles in fibre kilns.

An iron-rich body will promote rust break. See Cardew (Ref. No. 9) page 140.

Any factor promoting the development of the clay/glaze interface zone will promote rust break. This particularly applies to firing higher or soaking longer at top temperature, both these factors allowing the glaze to eat more effectively into the body. See Chapter 17 for a discussion of the factors affecting the clay/glaze interface.

3. Chun-blue Occurrence

Without the iron, the base glazes we are using are mostly what we have been calling limestone glazes or a limestone glaze with a little magnesia. Just as with limestone glazes (and others) a zone occurs on the alumina/silica chart where Chun-blue effect occurs, superimposed on the iron glaze typical for that area. In Experiment No. Fe2, for example, you may find, with suitable firing, a honey glaze at 0.3 Al_2O_3, 3.2 SiO_2, and a tenmoku at 0.4/4.2, both with a Chun-blue effect superimposed. One also gets teadust glazes showing Chun-blue effect in the same area of the alumina/silica chart.

4. Teadust Crystals

The teadust effect is the growth of green or yellow green pyroxene crystals in the glaze. It will be discussed in detail in the next section, but for now I will say that the teadust occurs typically in a reduced high iron glaze that contains a little magnesia (e.g. 0.1 - 0.3 M.P.) and is low in alumina. Under the right conditions, however, it may occur over a wide range of alumina and silica values. It is common to find teadust crystals in a honey or tenmoku background, but they will sometimes occur in a rust glaze as well.

SPECIFIC IRON GLAZES

Honey, Tenmoku, Kaki

The tests in the theory section (see previous section) would give you adequate occurrence of these three traditional glazes, especially if you have varied your clay and firing cycles as recommended.

If you have not done the experiments, you could choose glazes by reference to the Results Charts and get the recipes from the Data Sheet.

The following references also contain useful information:

1. The text by Tichane has a full discussion on traditional Chinese tenmoku-type glazes, and suggests an approach using a simple mixture of red clay and wood ash on an iron-rich body, fired in oxidation. See Reference 1.
2. The text by Wood (Ref. No. 2) has analyses and recipes for a number of tenmoku-type glazes. He gives recipes, but if you cannot get some of the materials, you can try converting directly from analysis to recipe (using your own materials) as he outlines in Chapter 6. If you cannot get the per cent analyses of any of your materials, use the Conversion factor listed in Appendix 10 of Fraser, or in the 'Table of mineral constants' in Hamer's Dictionary (Ref. 3) Page 338. For example, dolomite has conversion factors of:

0.304 CaO, 0.219 MgO. This means that theoretically pure dolomite yields 30.4% CaO, and 21.9% MgO by weight. The rest of the 100% is CO_2 and goes in the 'Loss' column in Wood's 'Percentage Method' calculation.

3. In Leech's *A Potter's Book* there are eight tenmoku-type glazes listed with comments, pages 170, 171. Where he uses 'medium ash', try almost any hardwood ash. Instead of 'reed ash', use any grass ash, e.g. bamboo, sugarcane, rice etc.
4. Hughan's recommendations (see Reference 4) are a good starting point for tenmoku and teadust glazes. He uses magnesia in his tenmoku glazes, whereas many potters prefer a simple limestone base (without magnesia) for the traditional black/rust tenmoku.

Oil-spot Tenmoku

The oil-spot tenmoku glaze is a spotted tenmoku glaze, with commonly a black tenmoku background, and spots of dark metallic sheen or rust. Some oil-spot glazes are easily obtained, but much depends on the firing and an excellent oil spot still represents a great challenge.

The generally accepted theory of 'oil spot' formation calls for a glaze with an overload of red iron oxide (Fe_2O_3) either in the glaze or in a slip under the glaze, fired in oxidation to cause a bubbling process after the glaze has melted. Hamer suggests that either two glazes, or a glaze over a slip, is necessary while Brother Anthony's approach requires just one glaze. These two approaches are given in detail below. Oil-spot recipes usually contain a lot of feldspar or nepheline syenite — at least 50%. One Japanese glaze authority told me that the oil-spot glaze was just a Shino glaze with iron oxide added. (Japanese Shino glaze is discussed later in the book.) The effect will often occur inadvertently when using a highly feldspathic glaze over an iron-rich slip fired in oxidation. The approach suggested by Brother Anthony usually gives a dark metallic (sometimes purplish coloured) spot, whereas using a glaze over a slip will often produce a rust-coloured spot. In both cases, the background is the usual tenmoku black.

Hamer (see Reference No. 3)

'The effect is achieved by the use of two glazes or one glaze over a vitrifying slip. Both glazes contain iron oxide but the one underneath needs to be overloaded with iron oxide. The overloading amount varies according to the glaze composition, but can be as much as 30% of the recipe. The top glaze needs to fuse first so that when the underneath glaze fuses and bubbles it does so through an already molten glaze. The top glaze holds the craters containing the underneath glaze and when the whole smooths out the oil spots remain.'

Brother Anthony (see Reference No. 5)

The following is a summary of the main points listed in the *Ceramics Monthly* article:

The basic oil-spot glaze consists of spots of magnetite (Fe_3O_4) deposited on the surface of a tenmoku glaze by a bubbling action.

The bubbling action is caused by the decomposition of red iron oxide to magnetite after the glaze has melted. This decomposition process occurs spontaneously at around 1230-1320°C in oxidation, or much earlier in reduction. (The decomposition is the 'reduction' of iron from Fe_2O_3 to Fe_3O_4):

$$3Fe_2O_3 \rightleftharpoons 2Fe_3O_4 + \tfrac{1}{2}O_2$$

Oxidation is essential, therefore, because if the decomposition occurs before the glaze has melted, no bubbles will occur.

The bubbles are the oxygen released in the decomposition process, and they come to the surface of the molten glaze bringing with them a minute amount of magnetite, which makes the spot.

The glaze must contain enough Fe_2O_3 so that not all is taken into solution as the glaze melts. It is the 'left over' iron that decomposes. It is necessary, therefore, to have a base glaze which favours the iron *not* dissolving in the glaze. From the 'Discussion of Results' earlier in this chapter you will realise that this will mean high alumina and silica and high alkali with low calcium (since calcium is very effective in dissolving iron). A high feldspar content obtains these requirements. To get the glaze to melt and smooth over at stoneware temperatures, a little Ca and Mg are necessary.

The iron oxide must be as pure as possible.

The glaze should be applied reasonably thickly. The thicker the glaze, the larger the spots. Thin glaze will often produce no spots at all.

With regard to molecular formula, Brother Anthony says, 'Findings indicate the following limits: 0.1 - 0.25 CaO, 0.15 - 0.35 MgO, 0.45 - 0.7 KNaO. The sum of these basic oxides will be equal to unity.

Al_2O_3 should have the same number of moles as KNaO*; SiO_2 should be 10 - 12 times that number of moles. Fe_2O_3 should be between 0.2 and 0.3 moles.'

Brother Anthony gives the Seger Formula for O.S.1 as a typical oil-spot glaze. I have added the oxide wt% and worked out three recipes using different sources of magnesia. The form of magnesia used by Brother Anthony is talc.

He suggests using a white clay body.

Other Oil-spot Glazes

Actually a wide range of high iron glazes will give oil-spot effects if thickly applied and fired in oxidation. Albany slip has been used for years to give oil-spot glaze. See the Data Box for O.S.2.

Another oil-spot glaze that is fairly easy to obtain is O.S.3. See the Data Box.

So you can see from the three formulae above that the oilspot phenomenon can occur over a wide range of iron glazes. It could be a waste of time therefore, to become too preoccupied with formula and recipe.

In view of all the preceding data, I would recommend the following program to obtain an oil-spot tenmoku:

Take one or more of the recipes listed previously (I would recommend O.S.I.) and try them. Use about 8% Fe_2O_3 in all tests (except O.S.3 which requires high iron) and apply the glaze thickly. Make multiple copies of each glaze to use the test firing approach outlined in Chapter 15, and some of these tests should be in the shape of draw rings, to be withdrawn from the spy-hole during the firing. Fire in oxidation, though in my experience, the best quality oil spot may not be in full oxidation — a gas kiln can sometimes give more lively results than an electric kiln. One problem you will have is smoothing over the glaze surface without losing the spots. It is standard procedure in Japan to use draw trials to determine the end of the firing. Some evidence of bubbling should be visible on the draw trials inside the kiln as maturity is approached. Pull out the first trial as the bubbling dies down. Usually the firing proceeds until draw trials show irregular spots on the surface. Temperature is then held and soaking proceeds until the desired quality is obtained.

Note: This implies that if you use feldspar as your source of KNaO, there will be no clay in the glaze. Note also that 'moles' is equivalent to molecular parts (M.P.).

O.S.1 SEGER FORMULA	OXIDE	WT%	RECIPES	A	B	C
0.6 KNaO	K_2O	11.4	K-FELDSPAR	64.9	64.9	66.1
0.15 CaO 0.6 Al_2O_3 6.0 SiO_2	CaO	1.7	WHITING	2.9	—	3.0
0.25 MgO Plus 0.2-0.3 M.P. Fe_2O_3	MgO	2.0	SILICA	28.1	28.1	24.6
	Al_2O_3	12.3	MAG. CARB.	4.1	1.6	—
	SiO_2	72.6	DOLOMITE	—	5.4	—
	Fe_2O_3	+8%	TALC	—	—	6.3
			RED FE OX.	+8%	+8%	+8%

O.S.2 SEGER FORMULA	OXIDE	WT %	RECIPES	A	B	C	D
	K_2O	5.3	ALBANY SLIP	100.0	—	—	—
0.2 KNaO	CaO	7.0	K-FELDSPAR		27.2	27.2	28.1
0.45 CaO 0.61 Al_2O_3 3.97 SiO_2	MgO	3.9	WHITING		11.0	2.5	11.4
0.35 MgO Plus 0.08 Fe_2O_3	Al_2O_3	17.3	SILICA		28.7	28.7	22.5
	SiO_2	66.5	KAOLIN		25.9	25.9	26.8
This is a typical formula for Albany Slip. Extra Fe_2O_3 must be added for oilspot. (Approx. 5%.)	Plus Fe_2O_3		MAG. CARB.		7.2	—	—
			DOLOMITE		—	15.8	—
			TALC		—	—	11.2
			RED FE. OX.	+5%	+8%	+8%	+8%

O.S.3 SEGER FORMULA	OXIDE	WT %	RECIPES	A	B	C
	K_2O	7.2	K-FELDSPAR	39.2	40.7	39.2
0.3 KNaO	CaO	4.3	WHITING	7.1	7.3	—
0.3 CaO 0.45 Al_2O_3 4.7 SiO_2	MgO	4.1	SILICA	36.7	30.3	36.7
0.4 MgO + 16% Fe_2O_3	Al_2O_3	11.7	KAOLIN	9.1	9.4	9.1
	SiO_2	72.7	MAG. CARB.	7.9	—	2.0
	Fe_2O_3	16.0	DOLOMITE	—	—	13.0
			TALC	—	12.3	—
			RED FE. OX.	16.0	16.0	16.0

Once you have the oil spots working, you can perhaps look at trying different raw materials, e.g. try soda feldspar instead of potash spar, try different sources of magnesia etc. Other colouring oxides can be added *with* the iron to try for different colour spots, but you should get the glaze working before you try this.

The Teadust Effect

The usually accepted definition of teadust is a tenmoku-type glaze with green or yellow-green crystals scattered through it. We may wish to keep this rather appropriate definition for 'teadust', but I would like to look further to the wider occurrence of this type of crystal in iron glazes.

A wide range of iron glazes will give the teadust effect with the right firing, and on the right body. A limestone glaze with a little magnesia (e.g. 0.1 - 0.3 MgO) would be a typical base. The magnesia is essential if the pyroxene crystals are to form. The figures for alumina and silica are much less important, though they do affect the size of the crystals, and if other factors are unfavourable (e.g. firing, clay type) then alumina in particular does become important. Low alumina favours formation of the crystals. There are lots of variables and it is impossible to explore them all at once, so I will take a few 'cross sections':

(a) Firstly, let us take a fairly straight forward iron glaze from Hughan's article: See the Data Box for T.D.1.

This glaze can be fired over a reasonable range, perhaps from Orton Cone 8 to 11. Under strict oxidation it will give a tenmoku; under strong reduction, a dark iron glaze; and even a dark blue-black in extreme reduction. With light reduction (neutral atmosphere?), however, it produces a typical teadust. The higher it is fired, the fewer teadust crystals appear. If barely matured, the crystals may be quite dense, and if the kiln is held at, say, 1050-1100°C for about an hour in the cooling, the crystals may completely cover the surface, giving a matt yellow-green glaze with no suggestion of tenmoku black. This is an important principle to note — the almost immature glaze giving dense crystal growth. It is probably because undissolved grains of silica are acting as seeding points. It should be possible to use this technique to develop a number of interesting matt colour glazes using pyroxene crystals, a combination of slight underfiring and soaking in the cooling cycle.

(b) Now let us take a glaze with more MgO and fairly low alumina and silica, such as the line blend used in Experiment No. Fe7 earlier in this chapter.

T.D.2 0.25 KNaO
0.45 CaO 0.25 Al_2O_3 2.5 SiO_2
0.3 MgO
+ Fe_2O_3: 0 - 20%

For more data, see Experiment Fe7 Data Sheet.

With this set of glazes, you will find the teadust effect occurring quite easily over a wide range of iron oxide contents and with a wide range of firings and clay bodies.

(c) I have mentioned the clay body several times. Some work we have done suggests that a rough clay will promote a

T.D.1 SEGER FORMULA	OXIDE	WT %	RECIPES	A	B	C
	K_2O	7.2	K-FELDSPAR	38.9	38.9	39.6
0.3 KNaO	CaO	7.1	WHITING	11.7	7.0	11.9
0.5 CaO 0.45 Al_2O_2 4.7 SiO_2	MgO	2.1	KAOLIN	9.0	9.0	9.2
0.2 MgO + 8% Fe_2O_3	Al_2O_3	11.7	SILICA	36.4	36.4	33.3
	SiO_2	71.9	MAG. CARB.	3.9	—	—
	Fe_2O_3	+8.0	DOLOMITE	—	8.6	—
			TALC	—	—	6.0
			RED FE OX.	+8%	+8%	+8%

T.D.3 SEGER FORMULA	OXIDE	WT %		RECIPES				
		1.5 SiO_2	3.5 SiO_2		with 1.5 M.P. SiO_2 A	with 1.5 M.P. SiO_2 B	with 3.5 M.P. SiO_2 A	with 3.5 M.P. SiO_2 B
				K-FELDSPAR	59.0	59.0	38.0	38.0
0.23 KNaO	K_2O	12.0	7.2	WHITING	28.6	21.7	18.4	14.0
0.62 CaO 0.28 Al_2O_3 x SiO_2	CaO	19.2	11.5	MAG. CARB.	5.8	—	3.8	—
0.15 MgO + 8% Fe_2O_3	MgO	3.3	2.0	DOLOMITE	—	12.8	—	8.2
	Al_2O_3	15.7	9.5	KAOLIN	6.0	6.0	3.8	3.8
where x = 1.5, 2.0, 2.5	SiO_2	50.0	69.8	SILICA	0.6	0.6	36.0	36.0
3.0, 3.5	Fe_2O_3	+8%	+8%	RED FE OX.	+8%	+8%	+8%	+8%

teadust under conditions that would normally not give crystals, e.g. Feeney's 30-mesh stoneware clay seems to promote teadust crystals. This may be, once again, the availability of seeding points provided by the grog or other rough material. I would recommend, once you get a teadust glaze working, trying it on all the stoneware bodies at your disposal.

(d) Different sources of magnesia will give different qualities of teadust.

(e) As regards the honey glaze with teadust, you might like to try the following line blend, which is a modification of an exercise suggested by Kado (Ref. No. 10). See Data Box for T.D.3. 1.5 M.P. silica gives a very runny interesting glaze at Orton cone 9, that is a honey with teadust in light reduction. Increase of silica stiffens the glaze up. A honey-teadust with a Chun-blue effect occurs when silica is about 3 M.P.

Tomato Red Glaze

These glazes are typically a fairly simple high iron glaze containing a high percentage of bone ash. Glaze No. 154 in deBoos (Ref. No. 6) gives tomato red with added iron oxide. The recipe and approximate formula are shown in the Data Box for T.R.1.

You will probably find the brightest colours in oxidation on porcelain.

Tessha

The tessha I am referring to here is a saturated iron glaze with spangles of haematite visible to the naked eye. It is common in a wide range of iron glazes as long as there is plenty of iron oxide, and an adequately slow cooling. Magnesia is not essential in the glaze, but the glaze T.S.1 (see Data Box) is a particularly handsome tessha that I have often obtained with reduction and arrested cooling.

Iron Glazes Using Natural Materials

Many iron-bearing rocks and clays will melt of their own accord, or with a little help from a flux, to give an iron glaze. An appropriate natural flux to try is wood ash. Rocks such as basalt will often give tenmoku type glazes with the addition of a little wood ash. Similarly, the old Chinese tenmoku glaze was apparently a mixture of a red clay and wood ash (see Tichane's book). There is a section on natural materials at the end of this book.

REFERENCES

1. *Those Celadon Blues* by Robert Tichane (The New York Institute for Glaze Research).
2. *Oriental Glazes* by Nigel Wood (Pitman).
3. *The Potter's Dictionary of Materials and Techniques* by Frank Hamer (Watson/Guptill).
4. 'High Iron Stoneware Glazes' by Robert Hughan in *Pottery in Australia*, Vol. 4 No. 2. (See following pages.)
5. 'The Chemistry and Physics of Oilspot Glazes' by Brother Anthony in *Ceramics Monthly*, October 1980.
6. *Glazes for Australian Potters* by Janet deBoos (Methuen).
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9. *Pioneer Pottery* by Michael Cardew (Longman Cheshire).
10. *Fundamentals of Glazes* (in Japanese) by Kado .

Soda feldspar	50
Silica	20
Bone ash	10.5
Calcite	6.5
Ball Clay QA or C	7
Talc	6
Red Iron Oxide	11

T.R.1
Approximate Formula

0.45 KNaO
0.3 CaO
0.25 MgO

0.5 Al_2O_3 5.0 SiO_2
plus approx. 10% Fe_2O_3
and 10% Bone Ash

T.S.1 SEGER FORMULA	OXIDE	WT %	RECIPE	
	K_2O	7.2	K-FELDSPAR	39.5
0.3 K_2O 0.45 Al_2O_3 4 SiO_2	CaO	7.1	TALC	6.15
0.5 CaO	MgO	2.1	WHITING	11.8
0.2 MgO + 12% Fe_2O_3	Al_2O_3	11.7	KAOLIN	9.2
Fire in reduction. To about Orton Cone 10. Soak in cooling cycle at about 1050-1100°C for 1 to 3 hours.	SiO_2	71.9	SILICA	33.4
	Fe_2O_3	+12%	RED IRON OXIDE	+12.0%

Ref. No.4: Extract from *Pottery in Australia*, Vol, 4 No.2, October 1965.
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HIGH IRON STONEWARE GLAZES

R.R. Hughan

Introduction

The traditional stoneware glazes variously called 'tenmoku', 'tessha', 'kaki', 'tea dust', 'hares fur', 'oil spot' and so on, all contain some 5 to 15 per cent iron oxide in alkali-lime-magnesia glazes maturing at temperatures higher than cone 8.

The wide variety of colours and effects observed in this family of glazes is due basically to (a) the amount of iron oxide held in solution, (b) the role which this dissolved iron plays in the glassy network structure, (c) the amount of Fe_2O_3 (hematite) which precipitates on cooling in the kiln and (d) the size and disposition of these hematite crystals, e.g., the 'hares fur' and 'oil spot' effects.

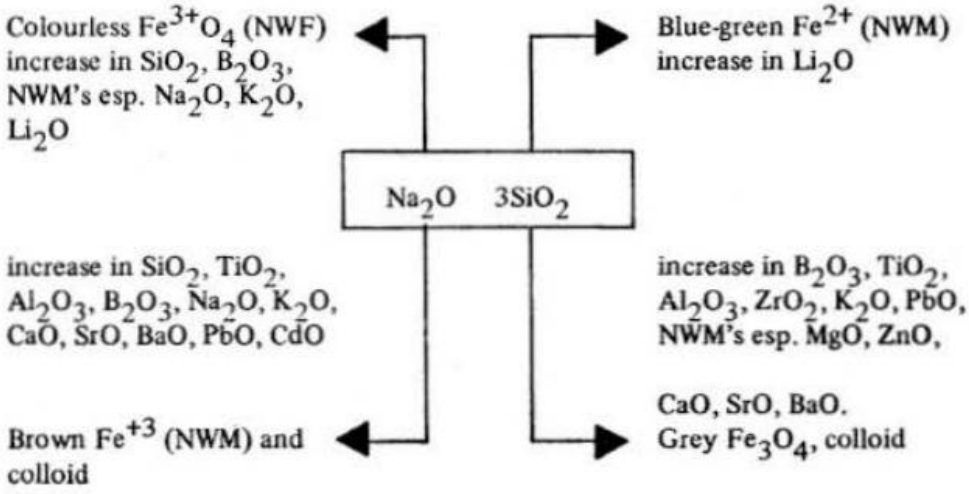
In this article we will not discuss these latter 'figured' glazes as their cause is still somewhat obscure. Interesting theories concerning them were proposed by Hetherington in his book, *Chinese Ceramic Glazes*, and this should be consulted for further details. We shall examine, in turn, the variables: glaze composition, iron oxide concentration, kiln atmosphere, and firing cycle; which largely determine factors (a) to (c) above. It will be necessary to assume that the reader is familiar with Zacharaisen's network theory of glassy structure and the concepts of network former (NWF) and network modifier (NWM). A discussion of these ideas will be found in any modern treatise on silicate glasses. The ideas which I have adopted concerning the role of iron in the glass structure are due to the Sheffield University school and differ somewhat from the German and Dutch schools, e.g., see Holdridge D.A., 'Ceramic Glazes', Craftsmen Potters Association, Newsletter No.12 (1964), p.36, for the German interpretation, and an account of Zacharaisen's ideas (p.28).

Iron in the Glaze Structure

According to the Sheffield school iron can exist in solution in glasses in three forms: (i) as $Fe^{3+}O_4$ tetrahedra replacing $Si^{4+}O_4$ tetrahedra, i.e., in the NWF position. In this form the iron is colourless. (ii) Fe^{3+} in the NWM position in which form it imparts a strong brown colour to the glass and easily aggregates to the colloidal (e.g. kaki) and eventually crystalline (e.g. tessha) forms. (iii) Fe^{2+} in NWM positions which may impart the blue green of celadons, alone, or may require the electronic interaction of a neighbouring Fe^{3+} to produce a visible colouration at the green end of the spectrum (this point has not been settled yet). Aggregation of Fe^{2+} and Fe^{3+} ions produces colloidal Fe_3O_4 (magnetite) in the glass, and this imparts a grey colour. All these forms of iron are present to a greater or less degree in iron-containing glazes, but the brown form tends to predominate over a wide range of compositions and firing conditions, and to mask all other colours. By special attention to composition, etc., it is possible to enhance the grey component at the expense of the colloidal brown form and thus to achieve the black brown known as tenmoku, but even in these glazes it is common (an aesthetically desirable) for the brown forms to precipitate at the edges where solution of body constituents has raised the alumina content of the glaze.

Glaze Composition

A general idea of the effect upon iron of the other glaze constituents is given by the Sheffield work on a simple glass, viz., $Na_2O.3SiO_2$. This is summarised in the diagram below in which the forms of iron which tend to increase with various additions to this glass, are shown.



It should not be inferred from this diagram that the bluest celadons will be obtained with the use of Li_2O in a glaze, since other factors intervene; notably the difficulty of reducing highly alkaline glazes.

Recent Japanese work on iron glazes (see *Pottery in Australia*, Vol.2, No.2, p.15 (1963)) has shown that MgO is especially potent in producing black glazes at the expense of brown*, but above 0.2 equivalents MgO tends to produce the crystalline glaze known as soba or tea dust. The crystals are of the diopside family ($CaO.MgO.2SiO_2$ – with Na+ replacing some Ca^{2+}, Fe^{2+} replacing some Mg^{2+}, and Al^{3+} replacing some Si^{4+}), and have a characteristic pale green tint.

A typical tenmoku glaze for an oxidising fire at about cone 9 was given as:

0.3 KNaO					
0.2 MgO	0.45	Al_2O_3	4.7 SiO_2	.....	A
0.5 CaO	+ 8%	Fe_2O_3			

For very fast firing cycles, e.g., in high temperature electric kilns a good black is:

0.3 KNaO					
0.2 MgO	0.35	Al_2O_3	3.5 SiO_2	.....	B
0.5 CaO	13%	Fe_2O_3			

My own tenmoku which is fired reducing is slightly lower in MgO and iron:

0.15	MgO					
0.65	CaO	0.5	Al_2O_3	3.5 SiO_2	.....	C
0.20	KNaO	6.5%	Fe_2O_3			

Iron Oxide Concentration

In all glazes a very high proportion of the iron is present in the colourless form, unless the glaze has been cooled slowly enough for Fe_2O_3 to crystallise out. In highly alkaline glazes the proportion may be as high as 75%, thus other things being equal, different compositions will require different amounts of iron to produce the same depth of colour. In theory the greatest density of colour is

*Note: This is not borne out by experiments in this Chapter; however the statement would need to be assessed in the context of the original article. I.C.

given by glazes high in CaO, MgO and Al_2O_3, but in practice it is found that iron oxide crystallises more readily from alkaline glazes hence they tend to be brown and opaque even at 4% to 5% iron, unless cooled rapidly. Increasing the iron content of a glaze tends to saturate it and thus promote crystallisation of the brown form, which masks all other forms.

Kiln Atmosphere

It is obvious that choice of either a reducing or oxidising atmosphere in the kiln will profoundly alter the proportion of the various forms of iron present. No systematic work has been done on this aspect so it is not possible to say how the colourless form of iron is likely to vary. It is safe to assume however that the blue-green ferrous and grey ferrous-ferric forms will increase under reduction, and the brown form will be favoured by oxidation.

An interesting side effect of reduction is observed in magnesia-containing glazes. Glaze A for example turns to tea dust under reduction, since the extra FeO produced supplements the MgO and enhances the crystallisation of diopside.

The effects of oxidation and reduction are only significant before and during the melting of the glaze. It has been shown recently that the solubility of oxidation of a previously reduced glaze only occurs at rims and similar thin patches.

Firing Cycle

High iron glazes tend to be fluid, and there is no real difficulty in dissolving 20% and more Fe_2O_3 in stoneware glazes at cone 10 or above, consequently the rate of heating of the glaze has little effect on its final appearance. The maturing temperature is important in two ways: firstly the colourless and blue-green forms are favoured by higher temperatures, and secondly if the glaze becomes sufficiently fluid to dissolve body constituents its composition is altered in the direction of higher Al_2O_3, which causes an increase in the brown constituent. This is most noticeable at thin patches, thus an overfired tenmoku frequently exhibits a banded appearance where throwing marks cause slight variations of glaze thickness.

The cooling cycle has the most profound effect of any of the variables on the final colour of the glaze. It is not just a matter of how many hours the kiln took to cool, but rather what the cooling rate was, during the periods when hematite (Fe_2O_3) crystals tend to nucleate, and then grow. This is the time when high iron stoneware glazes are still above 900°C or so. If no nuclei are allowed to grow the iron remains in solution and we get transparent green-browns to brown-blacks. If many crystal nuclei develop the resulting crystals will be small, and we get the type of opaque brown exemplified by kaki. If fewer nuclei develop and the crystals grow freely then we have the tessha-type glazes in which the spangles of hematite are visible to the unaided eye. The crystals tend to nucleate and grow from the glaze-body interface, hence thin patches of glaze appear browner than thick patches in cases where a tenmoku has been applied with varying thicknesses.

Conclusion

The firing cycle of no two kilns is alike, consequently every potter has to develop his own iron glaze by experiment. Iron glazes are unique in this regard, and herein lies one of their fascinations for the experimenter.

21 CELADON

If you look at a typical celadon recipe, you will see it is nothing but a simple lime/alkali glaze with perhaps one per cent of iron oxide, and fired in reduction. And yet there is a great mystique surrounding these glazes — a mystique that becomes understandable after you have seen a really good one and tried to do something the same. A good celadon is not easy to achieve, and it is a good vehicle for showing you how to integrate your understanding of glaze composition with the other inseparable factors of firing and clay body. Firstly, we will take a general look at the role of fluxes, alumina and silica, and then consider two particularly difficult types of celadon, the Lung Chuan, and the 'sky-blue' celadons and look at the approach suggested by Robert Tichane.

Tichane describes celadon with a mixture of romance and scientific analysis as follows:

> 'Celadon . . . The colour produced in reduced feldspathic glazes by low percentages of iron. Celadons are usually soft yellow-green colours because of contamination by titania. In the absence of titania, blues can be obtained which approach: "The blue of the sky as seen through rifts in the cloud after rain".'

THE BASE GLAZE — ITS ROLE IN CELADON GLAZES

The balance of fluxes, alumina and silica is critical in determining the colour response of the iron oxide. The following three experiments cover some of the more important aspects of the base glaze:

Experiment C(i) — Limestone Base Glaze

The following experiment varying alumina and silica gives a good introduction to celadons. You can prepare the 20 glazes by the volumetric blending of the corner glazes (glazes C1, C4, C17 and C20) or prepare the glazes individually from the recipes given. The base glazes have the same set of fluxes as the 0.7 Limestone Set.

Although ball milling is normal for celadon glazes, this can be left until introducing a particular glaze to the workshop as long as you use materials as fine as possible (and as finely sieved as possible) at this stage. The glazes should pass through at the very least a 120-mesh sieve, preferably 200-mesh.

Apply the glazes very thickly to individual tiles and assessment tiles made of porcelain or the kind of body suggested by Tichane for Lung Chuan (see later), for firing under different conditions as outlined in Chapter 15, under 'Test Firings'. Apply some of the glazes to draw trials — perhaps use small assessment tiles as draw trials to enable a large number of glazes to be drawn and compared simultaneously. If you decide you wish to study the two glazes from Tichane listed later, you will find that his 'Lung Chuan' is close to C10, and his 'Sky-Blue Celadon' is close to C18. You may wish to put these on the draw trials.

Fire under strong reduction, starting reduction around 950°C and mature the glaze very slowly. Try to take about 6 hours from 1150°C to maturity, removing the first draw-trial as soon as there is any sign of melting. (Hold a steel poker near the draw trial and see if the glaze shows reflections; a non-melted glaze will not reflect.)

Using draw trials and a pyrometer as your guide, hold temperature, soak, and slowly mature the glaze by soaking and carefully easing the temperature up. For the sake of maturing all the glazes, you might want to fire to about Orton Cone 9 or higher. This will probably be a bit high for a proper Lung Chuan; but if you have an assessment tile in a cold spot, or use the Lung Chuan on draw trials as indi-

cated, you should get the soft semi-opaque quality somehow, somewhere from your kiln. You should get a good range of different sorts of celadon from this experiment and some good Chun glazes as well.

The experimental data and typical results are presented below:

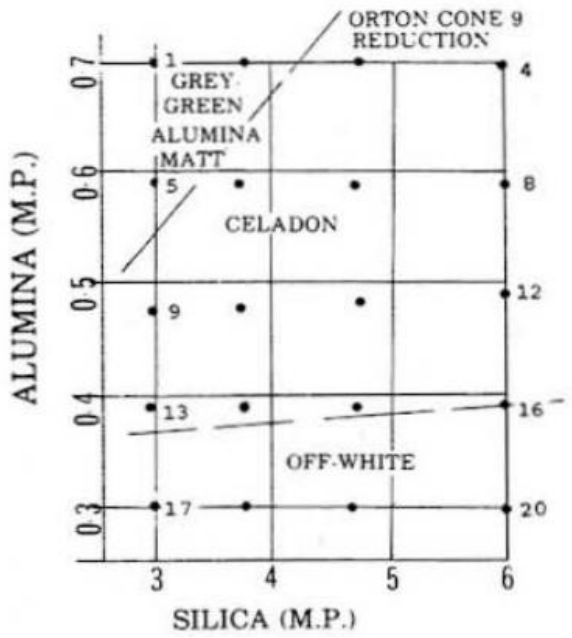
Limits of the Experiment:

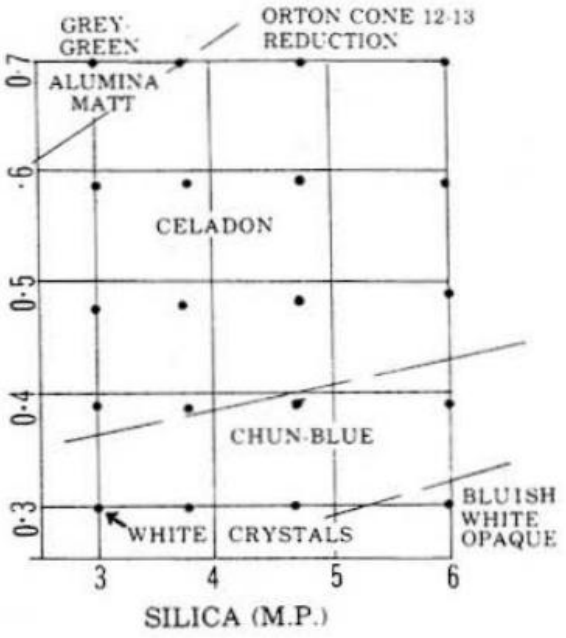
Seger: $0.3\ K_2O$ } 0.3 to $0.7\ Al_2O_3$
$0.7\ CaO$ } 3.0 to $6.0\ SiO_2$

Note: Add 1% Black Iron Oxide to each glaze.

	RECIPES				M.P.
	K-FELDSPAR	WHITING	KAOLIN	SILICA	Al_2O_3/SiO_2
C 1 (A)	45.83	19.23	28.34	6.60	.7/3.0
C 2	40.77	17.11	25.21	16.91	.7/3.75
C 3	35.72	14.99	22.09	27.21	.7/4.72
C 4 (B)	30.66	12.87	18.96	37.52	.7/6.00
C 5	47.87	20.09	21.26	10.79	0.59/3.0
C 6	42.43	17.88	18.91	20.87	0.59/3.73
C 7	36.98	15.52	16.57	30.95	0.59/4.70
C 8	31.53	13.23	14.22	41.03	0.59/6.00
C 9	49.92	20.95	14.17	14.98	0.48/3.0
C10	44.08	18.50	12.61	24.83	0.49/3.73
C11	38.24	16.05	11.04	34.69	0.49/4.69
C12	32.40	13.60	9.48	44.55	0.49/6.0
C13	51.96	21.81	7.09	19.16	0.39/3.0
C14	45.73	19.19	6.30	28.79	0.39/3.73
C15	39.50	16.58	5.52	38.43	0.39/4.68
C16	33.27	13.96	4.74	48.06	0.39/6.00
C17 (C)	54.00	22.67	0	23.33	0.3/3.0
C18	47.38	19.89	0	32.76	0.3/3.72
C19	40.76	17.10	0	42.16	0.3/4.67
C20 (D)	34.14	14.32	0	51.57	0.3/6.00

Results Charts:





Experiment C(ii) — Feldspathic Base Glaze

One effect of replacing calcium (from whiting) by potassium (from feldspar) can be seen by consideration of the grid-location diagrams in the Lime-Alkali series of base glazes in Part I; as feldspar increases, so does the minimum possible alumina and silica contents. One could overcome this if necessary by use of an artificial frit, but for this experiment we will accept the limitations inherent in using feldspar and whiting as the only flux ingredients.

Two important effects of moving from a limestone base glaze to a feldspathic one are that blues develop more easily, and it becomes more difficult to eliminate crazing. In general, the lower the alumina the better the blue, and the higher the alumina and silica content, the less the glaze crazes.

Make up glazes 32, 33 and 34 from the 0.6 Feldspar Set with 1.0% FeO added. Prepare, apply and fire the glazes as outlined for the previous experiment.

Experiment C(iii) — Barium Base Glaze

Tsuneshi Ishii of The Ceramic Laboratory, Department of Commerce and Industry, Kyoto, Japan, details some interesting experiments with high barium glazes being used to produce bright blue celadons. A wide range of glazes was tested and are described in detail in the article listed as Reference No.4. The following glazes are quoted as developing 'brilliant indigo blue':

0.5 K_2O
0.5 BaO 0.5 to 0.6 Al_2O_3 5.5 to 6.5 SiO_2

0.3 K_2O
0.7 BaO 0.45 to 0.5 Al_2O_3 5.0 to 5.5 SiO_2

(*Note:* The iron was added as ferrous silicate, 3.5 parts added to each 100 parts of base glaze.)

A problem with these glazes was wrinkling of the surface, apparently caused by physical properties of barium carbonate. Ishii overcame this problem by introducing the barium as barium silicate: 'Barium silicate, prepared by igniting a mixture of barium carbonate and silica to Seger Cone 11, was then ground fine and used instead of the carbonate alone. The result was very satisfactory and the defect of producing wrinkled surfaces was completely overcome. However, a glaze prepared with the barium silicate is apt to settle and solidify, making its use difficult.' The settling problem was overcome by adding seaweed glue to the glaze, ageing the slip, adding more glue, and then applying the glaze slip to the body with 'an ordinary brush'. *Note:* The correct proportions in the mixture to give barium silicate ($BaO.2SiO_2$) would be 62% barium carbonate + 38% silica.

To explore the function of barium in the development of a blue celadon, try the glaze given in the Data Box, suggested by Ishii as giving excellent results. The 'Alternative Recipe' is a lazy-potter's version of Ishii's. For all of Ishii's experiments on 'Kinuta Blue' celadon, the clay body contained 2% Fe_2O_3, and the iron was introduced to the glaze as iron silicate (see later under 'Blue Celadon'). Using the alternative recipe with 1% black iron oxide and applied to an iron-free porcelain (Podmore's) it is, however, possible to produce a good blue. This can be used as an easy starting point prior to trying things like barium silicate, iron silicate, and a suitable iron-bearing body.

LUNG CHUAN CELADON

The Lung Chuan celadon is a thick green to blue-green semi-opaque glaze with a soft semi-matt surface resulting from barely maturing the glaze in a long firing. It was made in great quantity in China over eight hundred years ago and was prized because of its resemblance to jade. It was exported from China, even so long ago, as far as western Europe, and by comparison with pottery made in Europe in those times, must have seemed

SEGER FORMULA	OXIDE	WT %	RECIPES	ISHII'S RECIPE	ALTER-NATIVE RECIPE
	K_2O	8.6	K-FELDSPAR	48.21	48.9
	BaO	14.0	SILICA	22.89	33.8
0.5 K_2O 0.5 Al_2O_3 6.2 SiO_2	Al_2O_3	9.3	BARIUM SILICATE	28.90	—
0.5 BaO Plus Iron Oxide	SiO_2	68.1	IRON SILICATE	3.5	—
	Plus Iron Oxide		BARIUM CARB.	—	17.3
			BLACK IRON OXIDE	—	1.0

almost magical. Even today, much of the magic remains — and without wanting to sound indecently eager — let's get into it.

We will start with Tichane's suggested recipe. See the Data Box (recipe from Reference No. 1, P. 52). In choosing the raw materials, remember the requirement of low TiO_2 if you want the blue colour. In particular, choose your kaolin carefully since many of our local kaolins are relatively high in titania.

Clay body: Tichane describes the correct clay body for this kind of glaze as a 'dirty' porcelain or a fine vitreous porcellaneous clay containing 1 to 2% of iron oxide, but here again, minimise titanium content.

Glaze preparation: It is standard practice to ball mill celadon glazes if one wants a result of refined quality. In particular, if you add the iron oxide as 'iron oxide', as opposed to introducing it in an ochre, or iron-bearing clay, then the glaze will need ball milling to prevent iron spots appearing in the glaze. On a smaller scale, if using 200-mesh bagged materials, you can prepare your glaze in the normal way, wetting it down and sieving, but instead of an 80 or 100-mesh sieve, coax it through a 200-mesh sieve. Most of the materials should go through easily; and material that refuses to pass with *gentle* brushing can be put into a mortar and pestle and ground for five or ten minutes until it will pass. If you are working with small quantities, it will not take too long, and you will be able to get quite good celadons without a ball mill. Note that a 200-mesh sieve is very fine and delicate, and material must not be *forced* through it.

Glaze application: The glaze needs to be thickly applied to achieve the Lung Chuan effect. Have it 2 mm thick on your test pieces. To get this thickness on pots without the glaze cracking or crawling can be a problem. If you have a spray gun (powered by a vacuum cleaner in reverse with the dust bag removed) multiple layers can be applied, or if using the dipping process, have the glaze mix fairly 'thick', or dip it several times. If using the multiple dipping process, the pot should be allowed to stand for only a couple of minutes between dippings so that the glaze does not dry out completely. The glaze should be firm, but not dry. The only way to test the glaze thickness accurately is to scratch or probe with a sharp point. Crawling caused by a high clay content in the recipe (e.g. kaolin) can be reduced by calcining part or all of the clay.

On your test tiles, have some impressed or raised texture, reasonably coarse to show through the thick glaze. Celadon excels in displaying this sort of decoration.

Firing: Fire the glaze in *strong* reduction, especially if you wish to get the blue tint. Tichane points out that the glaze must be underfired, for several reasons. Firstly, such a thick application of glaze would run off vertical surfaces if matured in the normal way. Secondly, the masses of bubbles that give the soft semi-opaque quality to a good celadon require that the glaze not be fully matured, lest the bubbles coalesce, giving fewer larger bubbles, in a shiny transparent glaze. Thirdly, normal maturing will remove the blue tint in a Lung Chuan type glaze. We have the problem, therefore, of how to smooth the glaze over to avoid the sandy, sugary texture present in most underfired glazes. This is overcome by using a very long maturing period to the firing. You can watch the progress of the smoothing out of the glaze by taking draw trials. Tichane says that if the glaze could normally be fired to Cone 8, thinly applied, to give a shiny green celadon, then you should fire to around Cone 6 with the same glaze thickly applied to get the softness of Lung Chuan.

LUNG CHUAN RECIPE (Tichane)	SEGER FORMULA	OXIDE	WT %
51 parts Feldspar	0.31 K_2O	K_2O	8.5
29 parts Silica	0.46 Al_2O_3 3.83 SiO_2	CaO	11.2
11 parts Kaolin	0.69 CaO	Al_2O_3	13.6
20 parts Limestone	plus 0.9% Fe_2O_3	SiO_2	66.7
1 part Hematite or Magnetite	or Fe_3O_4	Fe_2O_3 or Fe_3O_4	+0.9%

BLUE CELADON

Here are a few hints on developing the blue in celadon glazes:

1. Both Tichane and Wood (Refs 1 and 2) mention the importance of using materials low in titanium. Titania (TiO_2) develops greens and yellows at the expense of blue.
   Ishii (Ref. No.4) examined the effect of adding rutile to the following glaze (*Note:* This glaze is intermediate between glaze 19 and glaze 24 in the 0.8 Limestone Set):
   0.2 K_2O 0.4 Al_2O_3 4.0 SiO_2
   0.8 CaO plus 3.5% ferrous silicate
   In Ishii's experiment this glaze was giving an intense light green with some indigo colour. The effect of adding the rutile depended on the amount of addition as follows:
   0.05 - 0.10% rutile left the glazes still with indigo colour.
   0.2 - 0.3% produced bright grass green.
   0.4 - 0.5% gave yellowish green.
   0.7% gave a yellowish brown, 'like Yellow Seto'.
   Obviously quite small amounts of rutile can convert the blue to yellow. (It was in the context of producing a 'Tenriuji Yellow Celadon' glaze that Ishii experimented with additions of rutile, chrome oxide and manganous carbonate.)
2. The blue develops only in glazes with relatively low iron content. As iron oxide is increased, the glaze becomes more green.
3. The length of firing is important, in particular during the maturing of the glaze. Geoff Crispin (See Ref. No. 3) has demonstrated the importance of lengthy maturing to develop the blue. Strong reduction is necessary.
4. With a Lung Chuan type glaze, such as produced with Tichane's recipe, I have achieved subtle blues, but they seem to disappear as soon as the glaze is 'matured' in the normal sense, giving a green. As mentioned previously, this glaze needs to be smoothed over by time rather than temperature, to keep the blue. (Ball milling will make this process easier.) Tichane confirms this on page 48.
5. Work done by Lynne McDowell and Don Skoien working with me at the Queensland Potters' Association in Brisbane indicates that:
   (a) K_2O gives bluer glazes than Na_2O
   (b) Substitution of K_2O for CaO, keeping all other oxides constant, increases the blue.
6. Very blue celadons can be achieved where the iron blue is combined with the Chun-blue effect that occurs naturally in lime-alkali glazes low in alumina, with an alumina/silica ratio around 1:12. On page 102, Tichane gives a recipe for a 'brilliant sky blue' celadon with the following recipe:

RECIPE (Tichane)	
Potash Feldspar	49%
Silica	30%
Limestone	20%
Iron Oxide	1%
SEGER FORMULA (Approx.)	
0.3 K_2O 0.3 Al_2O_3 3.6 SiO_2 0.7 CaO + 1% iron oxide.	

   This glaze is typical of what I quoted for Chun glazes (See Chapter 18) and accounts for my statement that there is no sharp dividing line between Chuns and celadons. Compare Tichane's 'sky-blue' celadon recipe with his recipe for a Chun glaze (page 74). The glazes are virtually identical, the main difference being the 1% bone ash in the Chun.
7. Any attempt to obtain the mattness of Lung Chuan celadon by using the alumina matt effect will result in grey or brown tones creeping in, with no blue.
8. Japanese potters usually add the iron as iron silicate to help produce blues. The following detail from Ishii:
   'To prepare ferrous silicate, a mixture of ferrous oxide and silica compounded in the molecular ratio of 1:3 was ignited to Seger Cone 11, *i.e.* about 1320°C, with a reducing flame. The product was then washed thoroughly and ground fine.'
   (Note: Elsewhere Ishii quotes *ferric* oxide and silica in 1:3 proportion.)
9. A feldspathic base glaze (especially with K feldspar) can give reliable blues. See Experiment C(ii).
10. A barium base glaze can give very blue celadon glazes. See Experiment C(iii).

BUBBLES IN CELADONS

The semi-opaque quality of celadons is due to masses of tiny bubbles, barely distinguishable with the naked eye. If the bubbles get too large, the effect is lost. The main control you have over this is by underfiring *and using draw trials.* Apart from good luck, or years of experience with glaze and kiln, I know of no other way to achieve the fine firing control necessary, other than draw trials. If you look at sets of celadon glazes varying components like alumina, silica, fluxes etc., you will find at a given firing temperature, these factors do have an effect on bubble size and number. I feel, however, this is merely a reflection of the fact that the glazes are matured to different degrees. So in seeking to manipulate bubble size and number *in glazes of the type mentioned here,* I'm suggesting you can generally forget about glaze components and concentrate on glaze maturity as observed by draw trials.

REFERENCES

1. *Those Celadon Blues* by Robert Tichane (The New York Institute for Glaze Research.
2. *Oriental Glazes* by Nigel Wood (Pitman).
3. 'The Effect of Firing Conditions Upon the Colour and Quality of Celadon Glazes' by Geoff Crispin, in *Pottery in Australia,* 17/2.
4. *Experiments on the Kinuta Blue Celadon Glaze, Experiments on the Tenriuji Yellow Celadon Glaze* by Tsuneshi Ishii, transactions of the British Ceramic Society, Wedgwood Bicentenary Memorial Number, 1930.

22 KUAN GLAZES

DESCRIPTION AND THE PROBLEMS INVOLVED

Kuan Ware is another of the outstanding achievements of the Sung Dynasty Potters in China. The glaze itself is fairly simple. The difficulty in reproducing Kuan Ware accurately lies largely in the fact that the glaze has to be so thick to achieve the Kuan effect. To keep the overall thickness and weight of the pots reasonable, the Sung Potters made the body of the pot (i.e. before glaze application) very thin, e.g. 1 to 2 mm thick. Over this thin body, the thick strongly crazing glaze presented further problems outlined later.

Tichane (Ref. 1) gives an excellent account of Kuan Ware, and suggests some starting points for glaze and clay body.

Kuan glaze is usually pale blue or green, sometimes pale cream or near white. It is always thick, crackled (coarsely and heavily crazed) and opaque.

The body is dark coloured (with iron) and quite thin, 2 mm being typical. It is fine textured, and porous (not vitrified) containing a fair amount of free silica, apparently in the form of a fine sand.

Although the glaze is over a dark body, the overall effect is that of a pale translucent ceramic, this being largely due to the thickness and opacity of the glaze. The body does show through, however, on rims and high points to give a feeling of depth to the glaze. One can put the glaze on a pale body, of course, but the result is different, and probably does not rate as a true 'Kuan'. This is important, however, only if you are in the business of making replicas, and I will suggest you take both approaches, i.e. to make a proper Kuan and also to see what other interesting combinations we can find in this area by varying glaze and body compositions. You will find that a point I have been pushing all along is now coming home with a vengeance. You cannot really consider a glaze without discussing also the clay body it is to go on.

With traditional Kuan Ware, we have a thin (1-2 mm thick) clay body that is fine and dark coloured, and to get the Kuan effect over this body, the glaze must be quite thick — up to 2 mm. If the glaze is much thinner than this, the dark body will show through everywhere, and also the 'translucent' feeling will be lost. So we have the problem of how to fire this very thick glaze without its running off the pot. This is solved, as it was with the Lung Chuan celadon, by underfiring the glaze — barely maturing it, in fact.

Another problem is how to prevent such a thin pot from collapsing under the weight of the thick glaze, at stoneware temperature. This is managed by using a body that is still porous at stoneware temperature. The porous body solves another problem too: If you fire this kind of glaze thickly applied to a vitreous-firing clay body, you will find that when the thick glaze crazes, the craze line will continue into the vitreous body. If the body is thin, the pot will crack right through. If the body is thick, the glaze will lift right off in big spalls, pulling away a layer of the vitreous body. In a porous body, however, the craze fractures of the glaze will be dissipated and terminated amongst the pores of the body. (See Tichane, page 89.)

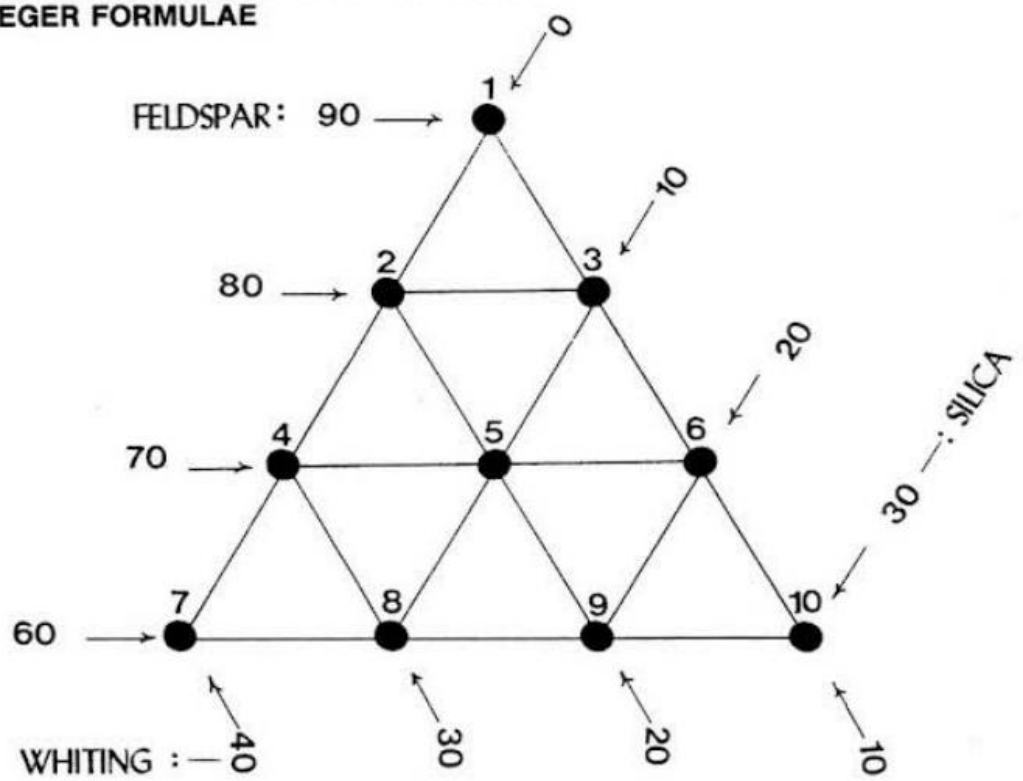
Another problem is obviously how to get a thick glaze layer onto a thin-walled pot. Tichane suggests a dip application, followed by several layers sprayed on. For this you will need a spray gun and a blower (e.g. back-to-front vacuum cleaner with the dust bag removed), or you may be able to make do with a hand-operated atomiser spray. For the purpose of testing, simply ladle the glaze on thickly and fire the test-tiles horizontally.

SUGGESTED RESEARCH PROGRAM

Glaze

Prepare the following triaxial blend of glazes. There are only ten glazes, so weighing the glazes individually may be as quick as volumetric blending. I put mine through a 200-mesh sieve (not essential) that required a bit of mortar and pestle work on the three corner glazes, which would probably make blending the quicker proposition. Diagram 22.1 shows the ten glazes represented by ten dots with the glaze reference number above each dot. With a little study, you will see how to work out the ten glaze recipes. Each recipe contains 100 parts, this being a mixture of feldspar, whiting, and (in most cases) silica. For example, glazes 4, 5 and 6 all contain 70 parts of feldspar. Glazes 6 and 9 both contain 20 parts of silica etc. For those wishing to use volumetric blending, but unable to work out a 'parts chart', see Diagram 22.2. This also shows the recipes of the three corner glazes.

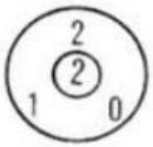
DIAGRAM 22.1 RECIPE TRIAXIAL AND SEGER FORMULAE



	SEGER FORMULAE			
GLAZE NOS.	K_2O	CaO	Al_2O_3	SiO_2
1	.62	.38	.62	3.71
2	.42	.58	.42	2.5
3	.59	.41	.59	4.22
4	.30	.70	.30	1.77
5	.39	.61	.39	2.83
6	.56	.44	.56	4.82
7	.21	.79	.21	1.27
8	.26	.74	.26	2.00
9	.35	.65	.35	3.18
10	.52	.48	.52	5.52

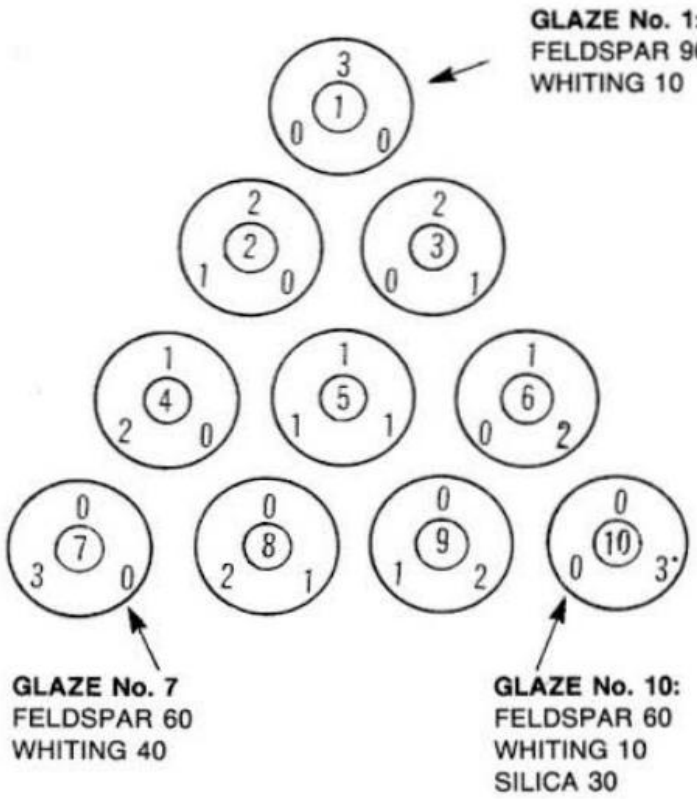
DIAGRAM 22.2 PARTS CHART:

KEY EXAMPLE:



GLAZE No. 2:
is made up of:
2 Parts of Glaze No. 1
1 Part of Glaze No. 7
0 Parts of Glaze No. 10

Note: To obtain pale blues, greens or creams, add 1% iron oxide to the glazes. Omit iron oxide for white glazes.



GLAZE No. 1:
FELDSPAR 90
WHITING 10

GLAZE No. 7
FELDSPAR 60
WHITING 40

GLAZE No. 10:
FELDSPAR 60
WHITING 10
SILICA 30

Note the total lack of clay in the glazes. Therefore, they must be kept well agitated during the blending to prevent the heavier particles settling out. This will also prove a problem if you decide to add a glaze of this sort to your range of workshop glazes, because they set like rock in the bottom of the container. You will probably need to use a suspender with them, if they are to be stored. (See the extract below from Hamer's *Dictionary* (Ref. 2).) Ball milling will usually help somewhat in suspending a glaze.

Hamer:

> *'Suspender.* An addition to a glaze slop to keep the materials in suspension. Popular suspenders are bentonite with calcium chloride and polymer adhesives. See *Flocculation.*
> Polymer adhesives help to bind a friable glaze to the ware before firing as well as providing slop suspension. Many other adhesives like gelatine, cellulose pastes and resin gums, temporarily thicken a glaze slop and keep it in suspension. However the most popular suspender is 1% bentonite which is flocculated by the addition of calcium chloride to the water.'

Have at least three assessment tiles of each clay body (one each for hot, medium and cold spots; or if your kiln fires very evenly, put tiles in different firings to obtain a range of temperatures).

Apply the glazes to the assessment tiles in the correct triangular order (make triangular assessment tiles if you wish). Make sure the glazes are quite thick -- at least 2 mm.

Clay Body

In initial tests you could try the ten glazes on any clays you have on hand. Try a white clay and a dark clay at least. Fire as detailed later.

For a second attempt, try to correct any shortcomings of the clays revealed in the first firing(s), and select, perhaps, just one or two glazes to work on. Tichane suggests 80 feldspar, 20 whiting (Glaze No. 2) as a good starting point. At the Queensland Potters' Association, we found Glaze No.5 (70 Feldspar, 20 Whiting, 10 Silica) a good glaze to work from. You may decide to try intermediate glazes — the steps in the triaxial blend are fairly large, and adjacent glazes can be quite different. But what I am suggesting is that, after the initial firing(s) of the triaxial blend, you should cut down the number of *glazes* you are working on to just one or two and put more effort into trying various *bodies*.

To obtain a reasonable 'Kuan Ware', you will probably have to develop your own clay body. I do not know of any commercially available body that fits all the

requirements. Using Tichane as a guide, you could compound a suitable body, i.e. fine, dark and porous. Or you might like to try one of the following starting points:

1. 100 parts dry Walker's No. 10(e.g. Turnings)
   5-10 parts red iron oxide
   Plus extra silica (10%, 15%, 20%....)
   Note: Ray Frost suggests the following body to give adequate iron, and prevent cracking:
   100 parts Walker's No. 10(dry)
   20 parts fine silica sand
   10 parts red iron oxide.
   (Ray's sand is equal parts of 30-mesh, 60-, 80-, and 200-mesh material; however, this is probably a coarser body than used traditionally.)
2. 40 parts kaolin (any brand)
   40 parts silica (200-mesh)
   20 parts feldspar
   5-10 parts red iron oxide
   Plus extra silica (10%, 15%, 20%....)
   Plus bentonite if necessary for plasticity.

Notes:

(a) Each of the preceding recipes represents several clay bodies with varying amounts of silica.

(b) The bodies should be made into slip with water and sieved as finely as reasonable possible (e.g. 100-120 mesh) to get rid of iron spots. If sand is to be added for any reason, introduce it after this sieving. The bodies should then be allowed to stiffen up to the plastic state so that test tiles, draw rings etc. can be made.

(c) As you increase the silica, the clay (after firing) will be more porous, and the glaze will be less crazed. Do not allow crazing to disappear completely. Use the photographs in Tichane's book as a guide to a typical Kuan crackle.

Firing

In initial tests, fire the test tiles horizontally. (When you get to putting the glaze(s) on pots, you may have to contend with the thick glaze falling off overhanging surfaces. Protect your kiln shelves. Perhaps try some glue in the glaze. This causes problems in glaze storage because of the tendency of the glue to set when exposed to air.)

As with the celadons, you need a long reduced firing, just barely maturing the glaze, using draw trials to tell you when it is adequately matured. When firing the triaxial sets, I would suggest the best glazes to use on draw trials are No. 2 and/or No. 5.

Have perhaps 6 assessment tiles (e.g. 3 each of the white clay and the dark clay, suggested in 'Clay Body') in 'hot', 'medium', and 'cold' spots.

Comments on Results

Many of the glazes seem to show a remarkably deep clay/glaze interface during the maturing process, or else there is some kind of sorting out of glaze particles before or during the firing. For example, Glaze No. 2 may be mature where it is ½–1 mm thick, and quite immature where it is 2 mm thick. You can observe this phenomenon on draw trials if you use Glaze No. 2. The glaze does not seem to go through an 'underfired matt' stage. It is either shiny or quite immature. The phenomenon seems to be typical of some lime (particularly *high* lime) glazes.

Virtually all the glazes with 20% or more whiting develop at least some mattness in the cooling process due to the formation of very fine crystals on the surface. For example, Glaze No. 2 when mature will show quite a shiny result on draw trials, but an adjacent draw trial that is not drawn but allowed to cool in the kiln, will be slightly matt. The cooling cycle is, therefore, going to be important in determining the surface quality of these glazes. The glazes with only 10% of whiting (nos 1, 3, 6, 10) seem to stay shiny in a normal cooling in a fibre kiln. Arrested cooling may (?) develop some mattness in these glazes.

The crazing or crackle gives a slightly complicated picture, depending on composition and glaze thickness. As one would expect though, high silica gives less crackle, e.g. Glaze No. 10 (with 30% SiO_2 in the recipe) has least crackle. It is possible to get a sort of 'double crazing' with very coarse crazing easily visible (and obvious to the touch) at 10-20 mm spacing, with minute crazing in between this visible only with a hand lens. I noticed this in some cases with Glaze No. 4.

The opacity seems to be due entirely to myriads of tiny bubbles, visible in most cases only with a hand lens. Some of the glazes (perhaps all?) will clear with full maturing of the glaze so that the 'Kuan effect' is lost.

REFERENCES

1. *Those Celadon Blues* by Robert Tichane (The New York Institute for Glaze Research).
2. *The Potter's Dictionary of Materials and Techniques* by Frank Hamer (Watson/Guptill).

23 SHINO GLAZES

TRADITIONAL JAPANESE SHINO

Although I am primarily concerned here with Shino Ware, it is worth pointing out that the Mino area, where Shino Ware evolved, is also responsible for three other distinctive traditional styles of pottery, namely Oribe, Black Seto and Yellow Seto. The four styles are closely interrelated, and it is fascinating to see how the Mino potters of four hundred years ago created such a wide range of wares from such a narrow range of materials. Although I find it a little hard to separate out just Shino Ware, I will nevertheless do this since the other three styles have received very little notice outside Japan, whereas so-called 'Shino' glaze is widely popular in Australia and overseas.

The origin of Japanese Shino Ware is somewhat obscure, but the following seems to be generally accepted. What the Japanese now call Shino Ware evolved about four hundred years ago in the Mino area, just inland from Nagoya. It developed apparently in an attempt to make a white ceramic. Prior to this, most of the pottery being made in Japan (especially in the nearby Seto) was rather earthy, using typically ash glazes, iron glazes etc. White pottery, however, was available from China and Korea, and this may have been an inspiration for the development of white Shino Ware.

There are several very famous old pots existing that are referred to as 'White Tenmoku'. These are believed to have been made in the Mino area and are regarded as precursors of the true Shino. (The 'tenmoku' refers here to the shapes, being typical shapes for pots bearing a tenmoku glaze.) The White Tenmoku appears to be a white, crazed feldspathic glaze, not unlike some glazes I obtained when working on Kuan glazes.

For example:

80-90% feldspar, 10% limestone, 0-10% silica

Although true Shino contains no limestone (it inhibits the 'fire colour', i.e. the burnt red where the glaze is thin), it is suggested in Fujioka's book that the original white glaze of the Mino area was obtained by 'altering the original ash glaze of Seto Ware by the addition of local feldspars'. The recipe I have given above could be equivalent to a feldspathic rock and wood ash.

Although one might have expected the Mino potters to try and emulate the refinement of the Chinese pots in their Shino Ware, this did not happen. At this time, Cha-no-yu (the Zen discipline that we call the Japanese Tea Ceremony) was gaining wide popularity in Japan, and Shino pottery developed under the influence of the Teamasters. From that time until this, the Teamasters have been arbiters of taste and have had a central influence in the field of Japanese aesthetics.

It would be incorrect to call Shino Ware unrefined. Aesthetically it is highly refined. The refinement has developed, however, in the opposite direction from that of, say, Chinese refinement, which ultimately was incorporated into industrial refinement, i.e. the refinement of modern industrial ceramics. It is this that I find inspiring about traditional Shino Ware, the way it defies virtually every rule in the book. The soft, asymmetrical, casual forms with their crazed, crawled and pinholed glaze, and the fragile, porous and often cracked body, all combine to form a united assault on accepted standards of excellence in industrial ceramics. Shino Ware defies what I call the 'machine aesthetic' that has indoctrinated us to prefer products that machines make best. According to this 'aesthetic', pots should be regular and even, preferably round, thin, and available in identically matching sets. The glaze should be refined and free of crazing, pinholes and other 'flaws'. The clay should also be refined and strong, preferably vitreous.

On this scale of values, Shino Ware (as typified by the traditional teabowls, waterjars etc. being made over the last four hundred years) would rate about zero out of ten! And yet these pots have always been highly prized. An appreciation of Japanese Shino Ware can be illuminating in our search for values that are relevant to artist/craftsman potters whose primary concern is the quality of their work, as opposed to businessmen potters, whose main aim is to maximise profit.

Traditional Shino Ware is usually classified into several types:

- Normal Shino or White Shino has a thick white semi-opaque crackled glaze over a white porous body. It sometimes exhibits 'fire colour' where thin, which may be anything from a faint pink to a burnt red.
  These wares were often decorated by brush with an iron pigment.
- Grey and Red Shino both result from the use of an iron-bearing slip under the normal Shino glaze. According to Fujioka (Ref. 1):
  'The distinctive tones ranging from deep grey to a lively reddish brown are brought about by variations in the percentage of iron in the slip, the thickness of the feldspathic glaze, and the firing procedure. The greater the iron content, the deeper the brown. Where the glaze covering is thick, the fired colour will be grey; where the iron slip filters through to the surface, there will be patches of red.'
  The term *Red Shino* refers to the rust-coloured or pink wares where the slip shows intensely over the entire piece. With both red and grey Shino Ware, decoration was often scratched through the slip to the white body.
- Another type of Shino is Marbled Shino, where a dark clay is marbled into the white with a normal Shino glaze over the top.

Although I spent a considerable time while in Japan studying Shino Ware, I experienced some difficulty getting useful information about modern good quality Shino. The following comments are from a variety of sources plus my own observations:

a. The bulk of the glaze is made up of one or more 'feldspars', usually soda or soda/potash feldspars. A 'feldspar' may be a feldspathic rock containing a fair amount of mineral silica.

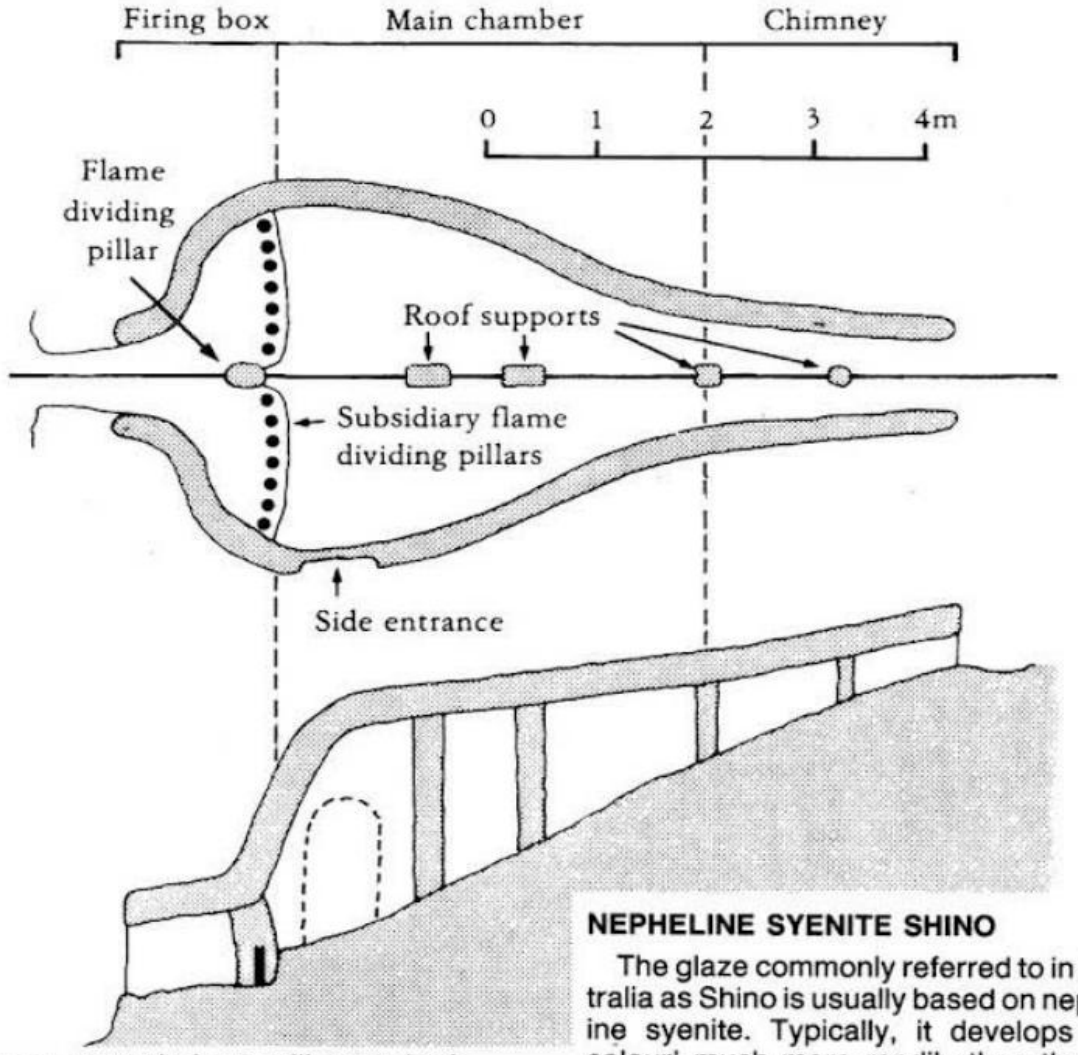
b. It is probable that the old Shino pots were raw glazed. The glazes were probably fairly low in clay (to obtain the results they did), however, which suggests they might have been applied when the pots were bone dry, so the glaze would not flake off when the pot dried and shrank. Glaze No. 1 (see later) was said to contain about 10% gairome, which is a clay used in glazes as we would use ball clay or some kaolins. In Brisbane, Mr Kenji Kato, gave a recipe (Glaze No. 2) containing 15%-18% Korean kaolin.

c. Small amounts of common salt and red iron oxide are sometimes added to the glaze, to aid the 'fire colour'.

d. With traditional Shino glaze, the materials are usually more coarse than we would normally use. In the case of Glaze No. 1, a small fraction of the glaze is larger than 40-mesh (and looks like silica grains). Sometimes part of the batch is ball milled, and part left coarse. This use of coarse glaze ingredients is apparently done for traditional effect, and, as long as the firing is reasonably prolonged at top temperature, is not rough to the touch. The visual and tactile effect is a fine, slightly granular surface. In the case of Glaze No. 2, Mr Kato recommends 60-mesh 'feldspar' be used. He also suggested the need for some glue in the glaze to help suspend the coarser particles.

e. A very long firing is normal. Traditionally Shino ware was fired in an 'ogama' (big kiln), a type of kiln that grew out of the earlier 'Anagama' (cave kiln). 'It was not built by digging a tunnel in the hillside or by roofing a deep trench as had been former practice. The floor was set a little way into the hillside and a wide arch, supported by three or four internal pillars, was built over it. Access was no longer from the firing box or chimney but from a side entrance. The most important improvements were in the firing box. On either side of the flame-dividing pillar there was a row of smaller pillars on top of which clay-filled saggars were set. Behind these there was a step up to where the floor of the main chamber began. More wares could be placed near the front of the kiln while the rows of pillars and the domed roof combined to create a partial down-draught. The overall result was that firing could be carried out more evenly and efficiently than had formerly been possible'. (Ref. No. 4) These

DIAGRAM 23.1 : Typical Ogama as used in the Mino Area in the 16th Century to produce Classic Shino-ware. Taken from Reference No. 4



kilns were nevertheless still very inefficient by modern standards for wood-fired kilns, taking a long time to fire and cool, and being incapable of a really 'hot' stoneware firing. These conditions favour good quality Shino. The long firing aids formation of the 'fire-colour', and presumably is also important in smoothing over the coarsely milled glaze. Also, if the glaze is fired in a more efficient kiln to a higher temperature, it comes out shiny and transparent. This is precisely what happened to Shino ware after the highly efficient 'noborigama' (climbing kiln) was introduced in early 17th century. Many Shino potters use ogama or anagama style kilns to make a modern imitation of the classic Shino quality. However, very good quality Shino is also produced commercially in (for example) gas kilns, using very long firings. (See technical details later.)

f. In traditional Shino, the clay body is always porous when fired. It is apparently a siliceous kaolinitic clay

NEPHELINE SYENITE SHINO

The glaze commonly referred to in Australia as Shino is usually based on nepheline syenite. Typically, it develops 'fire colour' much more readily than the traditional Shino. The following would be a typical glaze recipe:

70/80% nepheline syenite
30/20% kaolin
3% common salt

The higher the percentage of nepheline syenite, the shinier the glaze will be at a given firing temperature. At lower temperatures use more nepheline syenite and less clay to get the glaze to mature. The type and quantity of clay used in the glaze, and the glaze thickness, affects the quality of the crawling, which is often encouraged as a decorative effect. With a given glaze, the thicker the glaze application, the coarser the crawling pattern. The crawling can be reduced or eliminated by calcining some of the clay or by applying the glaze thinner (causing a possible tendency towards overall 'fire colour'), or by using less clay (causing the glaze to be shinier). The salt is not essential, but it does tend to heighten the fire colour, making it a darker burnt red.

'FIRE COLOUR' IN SHINO

The 'fire colour' is obviously a clay/glaze interface effect and seems to require a reduced firing with strong reoxidation and a *small* amount of iron in the clay and/or glaze. It is interesting to speculate about the role of salt in the formation of 'fire colour' in Shino glazes. As mentioned in Chapter 8, salt has the ability to volatilise iron from clays and glazes, in the form of ferric chloride. The following quotes from Parmelee (Ref. 2) are relevant:

> Under 'Volatilisation', page 205: 'Common salt in small quantities is sometimes added to the batch of a frit in order to bleach the same by reacting with some of the iron content of the raw materials; when heated, the iron forms the very volatile ferric chloride, and is quickly driven out.'
>
> Under 'Salt Glaze', page 318: 'It seems to be clear that chlorine set free in the salting action combines partly with hydrogen of the water vapour and partly with iron in the body, as sometimes indicated by the reddish coloured fumes escaping from the stack. Further, if a piece of white-burning clay is placed in the kiln, after the firing it will be found coated with a thin reddish glaze. Also, iron-stained sand used for setting of kilns is more or less bleached during the firing.'

This suggests the iron being removed from one site and deposited in another within the kiln. Perhaps this process is partly responsible for providing iron to the 'fire colour' zones, i.e. where the glaze is thin enough to expose the clay/glaze interface. Parmelee's 'fiery red glaze' (see Technical Notes later), which is apparently similar in composition to the 'fire colour' part of the Shino glaze, requires about 1.55% Fe_2O_3. Often this amount of iron could be accounted for simply by the glaze attacking the clay in the clay/glaze interface, where the glaze is over an irony clay, or iron slip. But often a good 'fire colour' is obtained over a relatively iron-free clay, and it may be that the volatilisation of iron by the salt also plays a role. If this is the case, the principle may be applicable to other glazes where the glaze and/or clay contain iron.

The glaze must be virtually free of CaO (and probably other RO fluxes too) if an intense 'fire colour' is to be obtained in the presence of very little Fe_2O_3. In Chapter 20 under 'Lime/Alkali Balance' it was pointed out that lime favours solution of iron oxide, while alkali fluxes (R_2O type) favour crystallisation — and it is minutely crystalline Fe_2O_3 that causes the 'fire colour'. Such small amounts of iron as are present would give perhaps a celadon, or honey glaze in a normal limestone glaze. But under the conditions present in the lime-free Shino glaze, it can produce 'fire colour' where the glaze is thin.

TECHNICAL NOTES

a. The analyses of a Shino glaze and clay body in the Data Box are of samples I obained from the Tajimi Ceramic Research Centre. The formula for the glaze, ignoring minor ingredients, is approximately:

$$\begin{matrix} 0.2\ K_2O & 1.2\ Al_2O_3 & 6.2\ SiO_2 \\ 0.8\ Na_2O & + 0.3\%\ Fe_2O_3 & \end{matrix}$$

(Alumina Silica ratio 1 : 5.25)

The original glaze was coarsely milled; some materials were coarser than 40-mesh. Also, some of the soda was present as salt.

(The author thanks Dr Ray Frost of the Chemistry Department, Queensland Institute of Technology, for analysing the above materials.)

b. Two nepheline syenite Shinos that I use are shown in the second Data Box.

A direct comparison of the Japanese Shino with the nepheline syenite Shinos is difficult because the former is coarsely milled, whereas my Shinos use 200-mesh materials. On the basis of the analyses and formulae, however, the Japanese Shino is relatively high in silica, the nepheline syenite Shino is relatively high in alumina.

My two recipes were developed from a recipe given to me by Doug Lawrie; I believe it originated with Len Castle.

c. Parmelee's 'fiery red' (Ref. 2, page 307).

Parmelee gives the following formula for a fiery red:

$$\begin{matrix} 0.8\ K_2O & 1.17\ Al_2O_3 & 5.35\ SiO_2 \\ 0.2\ Na_2O & 0.05\ Fe_2O_3 & \end{matrix}$$

This formula is examined by Cardew (Ref. No. 3) under 'iron red', and he shows how it may be achieved using nepheline syenite.

d. **Firing**

The following is taken from a kiln log used for producing high quality commercial Japanese Shino in Tajimi (gas kiln):

TAJIMI SHINO

	Glaze No. 1	Clay Body
SiO_2	64.2	78.23
Al_2O_3	20.3	15.56
Fe_2O_3	0.3	1.51
Na_2O	8.4	0.08
K_2O	3.08	1.16
CaO	0.15	.001
MgO	0.06	0.14
MnO_2	0.006	0.025
TiO_2	0.07	0.72
P_2O_5	<.0001	<.0001
L.O.I.	2.64	2.4

NEPHELINE SYENITE SHINO

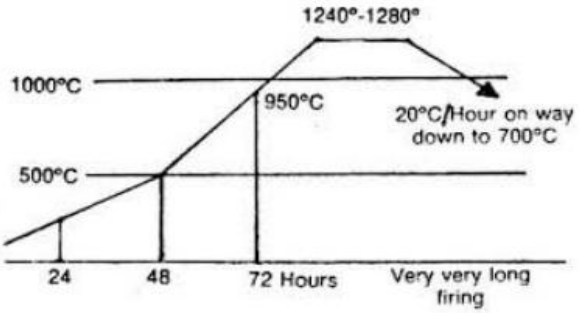
RECIPES		APPROXIMATE FORMULA	APPROX. OXIDE WT %
Nepheline Syenite	70	$0.24K_2O$	K_2O 3.8
Kaolin	30	$0.76\ Na_2O$ $1.75\ Al_2O_3\ 5.9\ SiO_2$	Na_2O 7.1
Salt	3	+ 3% NaCl	Al_2O_3 29.8
		(Al_2O_3 : SiO_2 = 1 : 3.4)	SiO_2 59.3
			NaCl + 3%
Nepheline Syenite	80	$0.24\ K_2O$	K_2O 4.3
Kaolin	20	$0.76\ Na_2O$ $1.4\ Al_2O_3\ 5.3\ SiO_2$	Na_2O 8.1
Salt	3	+ 3% NaCl	Al_2O_3 27.1
		(Al_2O_3 : SiO_2 = 1 : 3.8	SiO_2 60.5
			NaCl + 3%

0-950°C — 18 hours steady climb.
950-1200°C — Reduction. 14 hours steady climb.
1200-1220°C — Reduction. 12 hours soak.
1220-850°C — Oxidation. 41 hours firing down, adjusting gas pressure periodically to maintain steady temperature fall.
850°C Down — Cool naturally.

Note particularly the oxidation soak down to 850°C. With Shino-type glazes, including nepheline syenite Shino, the fire colour can often be enhanced by re-firing in a bisque.

Nepheline syenite does not require such an extended firing to produce the fire colour, but it does require a longer firing than normal. I would recommend a strong reduction firing, with about six hours spent above 1200°C. Most, or all, of this long soak could be in oxidation. A slow oxidised cooling should help the fire colour.

e. The following information from Mr Kenji Kato when he was in Brisbane is taken from the Queensland Potters' Association *Newsletter:*



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1. *Shino and Oribe Ceramics* by Ryoichi Fujioka (Kodansha Press).
2. *Ceramic Glazes* by C.W. Parmelee (Cahner Books).
3. *Pioneer Pottery* by Michael Cardew (Longman Cheshire).
4. *Shino and Oribe Kiln Sites* by R.F.J. Faulkner & O.R. Impey (Robert G. Sawers Publishing in Association with the Ashmolean Museum Oxford)

24 COPPER GLAZES

COPPER AS A COLOURANT

Copper may be added to a glaze in the form of copper oxide or copper carbonate ($CuCO_3$). There are actually two oxides, cupric oxide (CuO) and cuprous oxide (Cu_2O). Black cupric oxide is the one usually used for 'copper oxide'.The deep red or brownish cuprous oxide, however, is sometimes used. When seeking copper red or green or blue glazes, copper carbonate is usually used since copper oxide tends to give a speckle. $CuCO_3$ has less colouring power than CuO, if using equal weights, because the carbonate 'contains' CuO plus CO_2. A comparison of the molecular weights will allow an accurate substitution to be made:

Mol.Wt of CuO = 79.5
Mol.Wt of $CuCO_3$ = 123.5

Copper in glazes may exist in three forms: cupric oxide, cuprous oxide and metallic copper.

Cupric oxide is the oxidised form and is responsible for copper greens and sometimes blues, such as turquoise. Cuprous oxide is the reduced oxide and gives reds, but the extent to which this form of copper is present in copper reds is uncertain. It is generally accepted that copper red glazes owe their colour to minute aggregates of copper. Pure copper, when dissolved or dispersed as individual atoms, will not produce colour. However: 'When the copper forms aggregates of colloidal copper or metallic crystals, copper ruby is formed. As the aggregate or crystallite grows to larger sizes, livery or muddy colours result.' (Ref. Parmelee, page 472.)

OXIDISED COPPER GLAZES

Oxidised copper glazes will be green or blue, depending on the base glaze. In extreme conditions, a brilliant turquoise will result, but as conditions are gradually relaxed, the blue tends to green.

Basically, one needs a highly alkaline copper glaze, low in alumina to produce a blue. Sanders (Ref. No. 4, page 54) suggests soda, lithium and barium favour blues in oxidised copper glazes. As alkaline fluxes are replaced by, say, CaO, the blue tends to green. Similarly, as alumina is increased, the blue decreases. Silica helps, if anything, to stabilise the blue, and a siliceous body is apparently best for turquoise glazes.

Turquoise glazes are an interesting area for those firing in oxidation. As a starting point for experiment, I would suggest taking any alkaline frit (e.g. Ferro Frit 3110 or Podmore's Frit P.2250) and doing a line blend increasing silica e.g. 5%, 10%, 15%, 20% etc. The frit by itself will probably be very runny. The added silica should stiffen the glaze without loss of the turquoise. Perhaps a little bentonite (2%?) could be used to suspend the glaze without losing the blue. About 1% or 2% of copper oxide or carbonate should be adequate colourant.

We have noted previously that alkaline fluxes tend to be fairly volatile. Any firing condition that tends to decrease the amount of alkaline fluxes by volatilisation will tend to favour green rather than blue. For example, the higher the maturing temperature or the longer the firing, the greener will be the result.

Also, the colour green or blue may be lost by volatilisation of the copper oxide. See more under 'copper reds'.

For copper greens, a wide range of base glazes (with 1%-2% CuO) will suffice. This is another rich field for experimentation by those firing in oxidation.

For both blue and green copper glazes the colours are brighter over a white body unless, of course, the glaze is quite opaque.

REDUCED COPPER GLAZES — COPPER REDS

I find it very difficult to approach copper reds from a theoretical viewpoint because of the difficulty of relating information obtained from the literature to the results of practical experiments as a potter, this being compounded by the fact that much has been written on the subject, and much of it contradictory, especially as regards firing cycles. The problem as I see it is as follows:

Firstly, your 'copper red' may end up colourless for several quite unconnected reasons.

Secondly, there are several different qualities of red, which are obtainable with the same glaze, or different glazes, and which are strongly affected by glaze composition and firing conditions such as kiln atmosphere and time/temperature considerations. This is discussed further under 'Characteristics of Traditional Copper Red Glazes'.

1. Causes of Failure

The following are the main reasons why copper reds may fail to appear:

a. The glaze may not be adequately reduced, giving an oxidised copper glaze. If the content of copper were high (e.g. 1%-2% CuO) this should be obvious, as the glaze would be green. The most brilliant copper reds, however, usually have very little copper (e.g. 0.1% CuO) and this may be inadequate to give a noticeable green colour unless the glaze is quite thick.

b. The glaze may be too thinly applied. This is tied in with the next point.

c. Copper volatilises easily from glazes at stoneware temperatures, so the reason for lack of red may be lack of copper.

d. A 'striking' process is apparently involved. According to Parmelee (page 466) this accomplishes two things: 'Formation of copper nuclei and growth from the nuclei to the required size of crystallites.' Some glazes that have been adequately reduced and contain adequate CuO still fail to produce the red because of the time/temperature requirements in the firing to nucleate and grow the crystallites to the right size. In some cases, the nuclei are present (even though the glaze is transparent after the initial firing) and just require the right heat treatment for the red to appear. This might involve a second firing to around 800-900°C. Draw trials should prove useful in determining the best time/temperature treatment.

2. Characteristics of Traditional Copper Red Glazes

The following are the main phenomena that can be observed with the naked eye in traditional copper red glazes:

a. Red Colour

There seem to be two distinct forms of red. One is a deep transparent red, typical of 'sang-de-boeuf' glaze. Where thick, it may seem almost black; where thin it can be brilliant blood-red. The other is an opaque pink/red that occurs with the transparent red in most copper red glazes and that often gives the colour of sealing wax. It seems to play a large part in the 'peach bloom' glaze. It is probable that the transparent red corresponds to what Parmelee calls 'copper ruby', and the opaque pink/red to what he calls 'livery colour'. (Ref. Parmelee, page 472.)

b. Colourless Rim

Where the glaze is thin, on rim and other high points, the red gives way to colourless, transparent glaze. This is attributed to either:

Reoxidation of the red colloidal copper, turning it all into cupric oxide. (Ref. Heatherington, page 43.) Heatherington claims the glaze in this area is a very faint green, although I have not seen this.

OR

The copper is volatilised where the glaze is thin, leaving it colourless. (Ref. Herbert Sanders, No. 4, page 58).

The effect can be used most attractively to reveal raised decoration such as slip trailing, fluting etc.

c. Grey Colours

There seem to be two possible causes, both resulting from very strong reduction; firstly, the possibility of carbon inclusion, and secondly, the possibility, according to Norton (Ref. Parmelee, page 466), of too rapid growth of the copper particles causing black instead of red.

d. 'Flambe'

We observed in the section on Chun-blue glazes that many base glazes with the right proportions of alumina and silica have a natural tendency to produce Chun-blue at the right firing temperature. In

many copper red glazes, this effect occurs with the red, giving a mottled or streaked purple glaze known as 'flambe'. (See under 'Recipes' later.) The Chun-blue occurs independently of the copper; if the base glaze without copper is fired under identical conditions, a Chun-blue glaze will result.

e. 'Peach Bloom'

'The characteristics of the glaze comprise a soft pink effect with passages of deeper red colour and green spots occur in many examples' (Heatherington, page 49). In my experience, 'peach bloom' is associated with very strong reduction; it is possible that very early reduction may play a role in producing some of the mottling that sometimes occurs with 'peach bloom'. A comment from Parmelee in the chapter on 'Glaze Defects' may be relevant:

'Too slow watersmoking* accompanied by strongly reducing conditions results in the deposition of carbon particles in the unfused glaze. If this condition continues, the carbon particles penetrate deeply and the fusion of the layer accompanying the rising temperature locks the particles in the surface and the glaze has a grey or black colour. This effect is very pronounced when lead or copper is present in the glaze. Thorough oxidation, if not too late, restores the glaze to its proper appearance but the trace of carbon may remain in solution, giving it a faintly ivory colour.' (Parmelee page 585).

(**Note:* The term watersmoking usually refers to the first 100-200°C of the firing. I suspect in this case it could refer to higher temperature, basically any condition that is going to cause carbon to be trapped in the glaze.)

Heatherington says that the green spots that occur on some peach bloom samples are caused by... 'the oxidation of spots of metallic copper formed by the flocculation** of the colloidal metallic particles.'

**(Flocculation — The action of altering the physical properties of fine particles in a suspension so that they no longer repel one another but aggregate into larger particles, called 'flocs', and settle by gravity. The action is most noticeable with the colloidal particles of clay but other minerals are subject to the effect if the particles are sufficiently fine.' Definition from Hamer (Ref.9).)

I cannot claim to really know very much about 'peach bloom' at present, with the literature being somewhat confusing and results of experiments even more so. It seems to me, a good quality peach bloom is a chancy thing with marginal effects that are hard to control.

3. A Summary of Facts and Opinions on Copper Reds

The conclusions listed below are compounded of readings from the literature (particularly Parmelee and Heatherington) and results from work done by some members of the Queensland Potters' Association glaze group. I would like to draw your attention to *Reds, Reds, Copper Reds* by Robert Tichane (Ref. No. 9), recently published, which sheds some new light on the subject. Our starting point at the Queensland Potters' Association was a glaze I have used for many years which is derived from Norton (Ref. No.3, page 248). See Data Box.

a. It would seem that the size of the copper particles suspended in the glaze has a marked influence on the quality of the red, finer particles giving a brilliant transparent red, coarser particles giving opaque pink/red. (e.g. See Parmelee, page 465, also page 472).

Table 24.1 lists several factors that seem to influence this balance between the two types of red. One should not conclude from this that the same effect can

RECIPE (NORTON)		SEGER FORMULA			OXIDE	WT%
Ferro Frit 3191	13.0	0.4 Na_2O	0.35 Al_2O_3	3.79 SiO_2	Na_2O	7.4
Whiting	14.0	0.6 CaO		0.19 B_2O_3	CaO	10.0
Soda Feldspar	44.0		+ 0.2% CuO		Al_2O_3	10.6
Tin Oxide	1.0		1.0% SnO_2		SiO_2	68.0
Cupric Oxide	0.2				B_2O_3	3.9
Kaolin	3.0				CuO	+0.2%
Silica	25.0				SnO_2	+1.0%

TABLE 24.1

Favouring Transparent Red (Smaller Copper Particles)	Favouring Opaque Pink/Red (Larger Copper Particles)
Low Copper Content (e.g. 0.1% CuO)	High Copper Content (e.g. 1% CuO)
High B_2O_3 (e.g. 0.3-0.4 M.P.)	Low B_2O_3 (e.g. Zero)
High Alkali (e.g. 0.6 KNaO)	Low Alkali (e.g. 0.2 KNaO)
Some Tin Oxide	Zero Tin Oxide
Moderate Reduction	Strong Reduction
Low Alumina	High Alumina

be had by e.g. lowering copper content *or* by raising B_2O_3 content. Work done by Lyndal Moor shows that increasing B_2O_3 up to a point will cause the production of a fairly reliable ruby red (almost black) glaze. In trying to achieve the same effect by reducing copper, the glazes seem to go colourless before that intensity is obtained. Incidentally, Lyndal's work shows that continued addition of B_2O_3 to the copper red glaze will result in a deeper and deeper red, giving way abruptly to a colourless or greenish glaze.

Though I have always used tin oxide in my copper reds, I have not tested its role in producing one or other of the two types of red. Good reds can be produced without tin oxide; however, the literature suggests tin oxide has a role in keeping the copper particles small (see Parmelee, page 468) so, theoretically, tin oxide should favour the transparent red rather than the opaque pink/red.

b. For brilliant copper red colours, use a fine white clay body, preferably porcelain. Any significant amount of iron in the body will tend to give muddy beetroot colours. Heatherington suggests (page 50), however, that a small amount of iron may have been present in Chinese peach bloom glazes.

c. For brilliant reds, the glaze needs to be well matured to clear it of bubbles.

d. Magnesia in the glaze will produce pinks, including matt pinks. Brilliant reds are difficult if not impossible in a magnesia glaze.

e. As mentioned before, the glaze will be colourless if it is too thin. *Note* that a glaze with 0.1% CuO will probably need a thicker application than the same base glaze with, say, 1% CuO, for the colour to appear.

Also, extended firings will tend to burn out the copper, leaving a colourless glaze.

f. Alumina and silica variations seem relatively less important than flux variation, though high alumina glazes favour pink rather than red. Variation of alumina and silica do, however, have the normal effect with respect to producing matts (e.g. high alumina) Chun-blue ('flambe'), runny, stiff glazes etc.

g. Soda seems to favour more brilliant reds than potash. As mentioned in the list, high KNaO seems to favour the dark transparent red, but it possibly also favours grey (with the red) in strong reduction.

h. Considerable work has been done on using local reducing agents in the glaze to obtain reduction of the glaze in an oxidation firing. A very fine grade of silicon carbide (e.g. 200 mesh) is what is usually used. It can also be applied in a slip under the glaze, giving the possibility of getting controlled red and green from copper in the same firing. Something between 0.2% and 1% SiC would suffice when mixed into the glaze.

4. Firing

The firing cycle is quite important in the production of copper red glazes. A glaze such as Norton's (given before) can give a wide range of effects simply by changing the firing. It is in this area that potters seem to differ most extremely. Some have most elaborate firing cycles. My own is fairly simple: I reduce strongly from about 900°C or 950°C until approximately 1230°C, then soak and oxidise until maturity is reached. Some potters start reduction very early (e.g. 650°C), some late (e.g. 1200°C, some reduce for long periods, some for a very short period. One problem in assessing firing cycles is that many kilns start reducing of their own accord, and a potter who claims to start

reduction at 1200°C may find that in fact the kiln starts reducing by itself much sooner. Reduction meters are now readily available, though still expensive, and these should eventually take a lot of the guesswork out of these matters. Some potters claim to be able to turn an oxidised copper glaze into a copper red in a reduced re-firing to a low temperature, e.g. 700-800°C. (One author using this process, F. Carlton Ball, says however that the red can be abraded off — it is just on the surface). And then of course there is the phenomenon of 'striking', which indicates that a colourless reduced copper glaze may be made to produce red by re-firing to a relatively low temperature.

An obvious starting point for someone wanting to try copper reds is to put samples of, say, the following recipes in their normal reduction firing, and see what happens.

5. Recipes

a.

Cesco Frit 2	13
Whiting	14
Soda Feldspar	44
Tin Oxide	1
Kaolin	3
Silica	25-35
Copper Carbonate	0.2%-0.1%

This is the recipe I use, derived from the Norton recipe given earlier. Depending on firing conditions, it will give a range of results, including 'sang-de-boeuf', 'flambe' and 'peach bloom'. Use the higher percentage of silica for 'flambe'. Many copper red glaze recipes will easily give 'flambe' by just adding extra silica. This can be understood by consideration of the location of the glazes on the alumina/silica chart in relation to the Chun-blue zone.

Beryl Taylor has had considerable success with Norton's recipe, substituting a range of frits weight for weight in the recipe instead of the Ferro Frit 3191.

b. The Data Box shows some Seger formulae taken from Lyndal Moor's work. I have calculated corresponding oxide wt.% and recipe figures.

SEGER FORMULA (MOOR)	OXIDE	WT %	RECIPE	
'BLACK RED'	Na_2O	6.8	Frit 3134	36.9
0.36 Na_2O 0.32 Al_2O_3 3.5-4 SiO_2	CaO	10.9	Na Feldspar	22.7
0.64 CaO 0.42 B_2O_3	Al_2O_3	9.9	Whiting	5.4
+ 0.5% $CuCO_3$	SiO_2	63.7	Kaolin	12.7
1% SnO_2	B_2O_3	8.8	Silica	22.3
	SnO_2	+ 1%	SnO_2	+1%
	$CuCO_3$	+ 0.5%	$CuCO_3$	+ 0.5%
'FLAMBE'	Na_2O	7.2	Frit 3134	21.2
0.36 Na_2O 0.25 Al_2O_3 3.5-4 SiO_2	CaO	11.6	Na Feldspar	39.2
0.64 CaO 0.23 B_2O_3	Al_2O_3	8.2	Whiting	12.0
+ 1% $CuCO_3$	SiO_2	67.8	Kaolin	0.4
1% SnO_2	B_2O_3	5.2	Silica	27.2
	SnO_2	+ 1%	SnO_2	+1%
	$CuCO_3$	+ 1%	$CuCO_3$	+ 1%
'PINK'	Na_2O	5.7	Frit 3134	10.1
0.36 Na_2O 0.5 Al_2O_3 4.5 SiO_2	CaO	9.2	Na Feldspar	36.4
0.64 CaO 0.14 B_2O_3	Al_2O_3	13.1	Whiting	11.7
+ 1% $CuCO_3$	SiO_2	69.5	Kaolin	12.9
1% SnO_2	B_2O_3	2.5	Silica	28.9
	SnO_2	+ 1%	SnO_2	+1%
	$CuCO_3$	+ 1%	$CuCO_3$	+ 1%

Note: A couple of high B_2O_3 frits that should prove useful in adjusting B_2O_3 contents of copper reds are:

Ferro Frit 3271

0.514 Na_2O

0.768 B_2O_3 2.255 SiO_2

0.486 CaO

M.WT : 248

Ferro Frit 3134

0.316 Na_2O

0.632 B_2O_3 1.47 SiO_2

0.684 CaO

M.WT : 191

For other frits that may be useful, see 'Technical Notes for the Craft Potter' by Russell Cowan Pty Ltd.

c. Two Janet de Boos recipes (Ref. No.8)

152	Potash Feldspar	55
	Calcite (Whiting)	25
	Silica	15
	Frit3110	5
	Tin Oxide	3
	Copper Carbonate	0.5
153	Potash Feldspar	48
	Silica	24
	Calcite	16
	Kaolin	5
	Barium Carbonate	4
	Frit 3110	3
	Tin Oxide	3
	Copper Carbonate	0.5

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2. *Ceramic Glazes* by Cullen W. Parmelee (Cahners Books).
3. *Ceramics for the Artist Potter* by F.H. Norton (Addison-Wesley).
4. *Glazes for Special Effects* by Herbert Sanders (Watson/Guptill).
5. *Glazes for the Craft Potter* by Harry Fraser (Pitman).
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7. 'Studio Potter'. A number of articles by the following authors:
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   Laura Andreson
   Tom Coleman
   Jean Mann
   George Wettlaufer
   F. Carleton Ball
   and also selected abstracts.
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25 NATURAL GLAZE from WOODFIRING
The Effects of Flame and Ash

One type of pottery that fascinated me in Japan was their natural ash glaze wares — a style of pottery that has been made for centuries there, utilising the effects of fused and melted ash, and fire marks, on pots that are placed unglazed in a wood-fired kiln. An interesting point about the history of Japanese pottery is that, unlike other countries, where pottery styles evolved with advancements in ceramic technology and earlier styles died out, in Japan most of the more technologically primitive styles continued to flourish side by side with the more advanced. The influence of *cha-no-yu* (tea ceremony) has undoubtedly been important here with its preference for natural and simple means.

If you look back far enough into Chinese and Korean pottery history, you will find pots with natural ash glaze — the ash from the fire landed on some parts of pots that were near the firebox or burning zone; and if the temperature were adequate, the ash would melt to form a natural glaze in patches and dribbles on the pots. Vapour effects from the wood also mark and colour the clay. Most wood ashes contain enough of the right ingredients to give a melted glaze at stoneware temperature.

In Japan there has been a continuous tradition of making this type of ware for many hundreds of years in centres such as Bizen and Shigaraki. There were originally six centres where this type of wares was made, including Bizen, Shigaraki, Iga, Tamba, Tokoname and Echizen. The tradition seemed to be most strongly matured in Bizen and Shigaraki when I was there in 1972, and I spent some time studying the natural ash-glazed ceramics of these two areas in particular. I had a workshop in Shigaraki for six months, and participated in wood firings there and in the Bizen area, and I feel there is something to be learned by a comparison of the approaches used in the two areas.

Perhaps the most important difference between the two was that virtually all Bizen potters purposely extended their firings for a week or more to get ash and flame effects as far through the kiln as possible. In Shigaraki most of the natural ash glaze pottery produced while I was there was done without unduly extending the firing; most of the kiln was actually packed with glazed pots in the normal manner; and only a small volume, right next to where the wood landed in the kiln, actually produced the ash and flame effects. I believe, however there has been an increase in the use of anagama kilns with extended firings in Shigaraki in recent years. The clays used in the two areas are quite different. In Bizen, the clay is dark with iron, and mostly of very fine texture with perhaps a few small stones in the clay; but the overall effect is of a fine, plastic, dark clay. The Shigaraki clay used for flame and ash marked pots is by contrast a white kaolinitic clay with lots of coarse stones of silica and feldspar, stones perhaps 3 mm (1/8") or larger, in diameter. But the point I would like to make to Australian potters wanting to work with wood firing to get a natural ash glaze effect is that this type of pottery is possible in any stoneware wood-firing in positions close to the firebox.

The problem for anyone making a living from pottery is that this style of pottery is very hard to produce in quantity and has a very limited demand. They tend to be 'potters' pots', the general public still feeling a bit uneasy with unglazed surfaces and some of the rough effects obtained in this way. So economic considerations may dictate that Bizen style firings are out for most of us, but most wood-fired kilns can produce some ash and flame marked pots in or near the firebox in zones often left empty anyway. The only real cost in using these areas of the kiln is that pots placed there suffer a high mortality because of the mechanical and pyrotech-

nical problems involved in having pots so close to the firebox.

TYPICAL SHIGARAKI CLIMBING KILN
(See Diagram 25.1)

In Shigaraki, the climbing kilns are commonly twelve or more chambers, climbing up a hill, though these days they usually fire only the first few chambers. No external chimney is required as the climb from first to last chamber is adequate. The firebox may be fired for around two to three days until the first chamber is red hot. Side-stoking of the first chamber then starts and continues until temperature is reached, as indicated by cones and/or draw trials. The stokeholes are then sealed up and sidestoking starts on the second chamber, which should also be at about red heat by now; and so it proceeds up the hill. The sidestoking of each chamber may be a matter of one or two hours, or over a day, depending on the kiln, the stacking and the desired effect. The air for combustion of side-stoked wood comes mainly from air sucked through the mouth of the firebox, and up through the previously fired chambers, passing through the vent-holes that interconnect the chambers. This causes a rapid drop in temperature after a chamber is matured and the stoke-holes sealed off. As the air passes up through the kiln cooling the preceding chambers, the air becomes super-heated, and the dry pinewood fuel explodes into flame immediately it hits the floor.

Traditionally the pots showing natural ash glaze effects are packed in Zone A (See Diagram 25.1). Interesting effects, however, are to be had by stacking pots in the vent holes (B) or along the back wall of the firebox (C). The Zone D on the back wall of each chamber beneath the vent holes is a dead spot which is relatively cool, and usually no pots at all are packed here. Zone E contains the bulk of the pots, which have glazes applied in the normal manner.

USING A SMALLER KILN

Very similar results to those described above can be had in a standard small wood kiln such as the one described by Janine King and Stephen Harrison in their booklet, *Layed Back Wood Firing* (See Diagram 25.2). Pots can be stacked on the floor of the firebox, especially to the rear in the throat arch area (Zone X), and also where a bag wall would normally be (Zone Y). A lattice bagwall may be used with pots in the holes, or no bagwall at all, if this can be done without upsetting the flamepath. This involves no major modifi-

DIAGRAM 25.1 : SHIGARAKI TRADITIONAL CLIMBING KILN

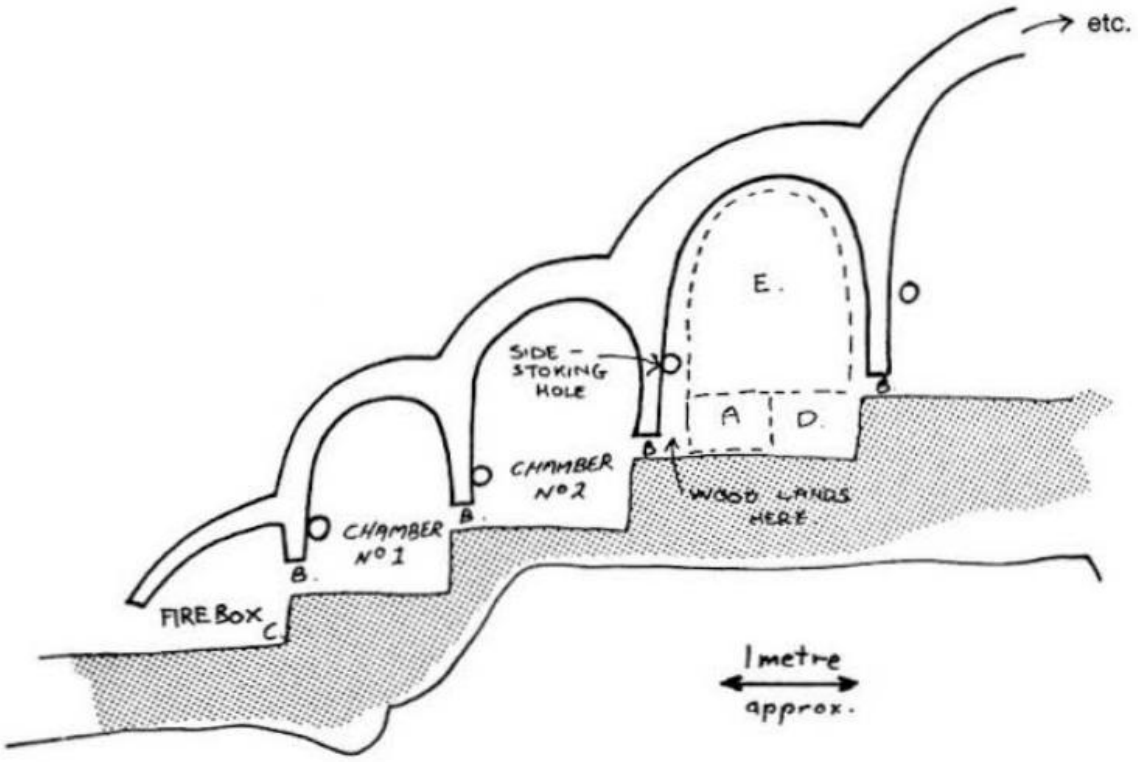
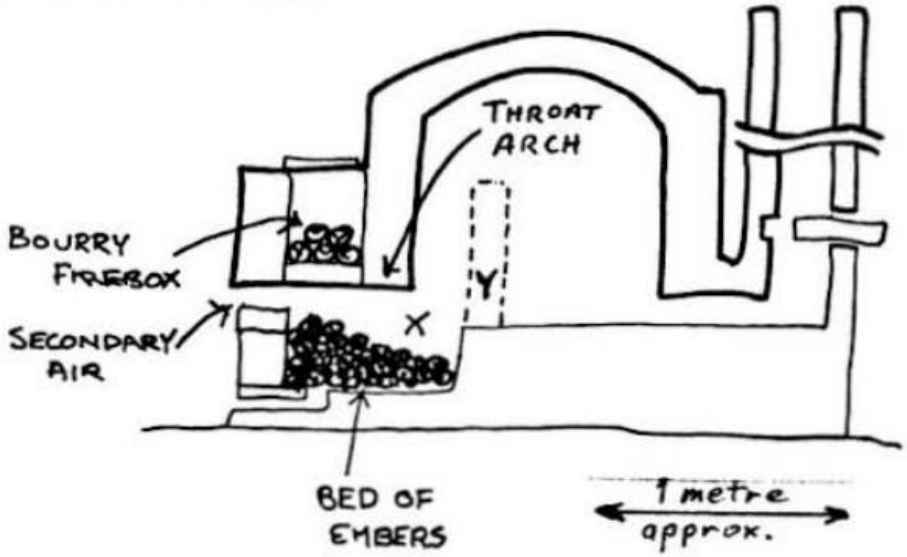


DIAGRAM 25.2 TYPICAL SMALL WOOD-FIRED KILN (30 cu. ft.)
as per J. King and S. Harrison.)



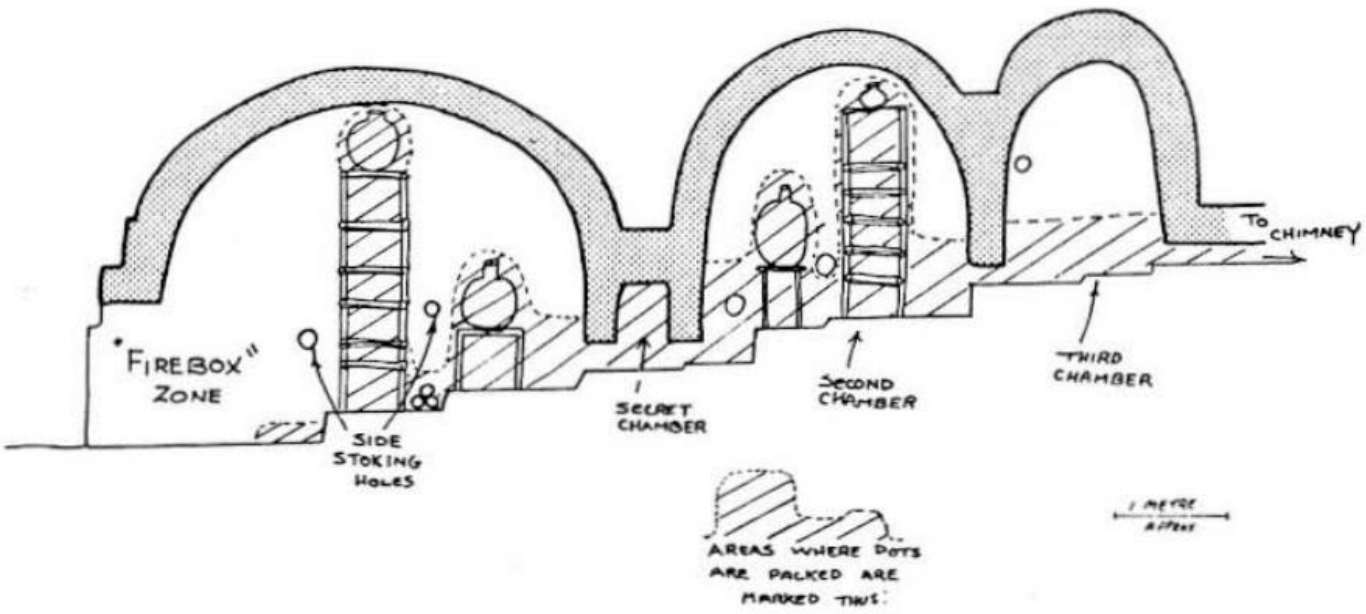
cation to the kiln. If the temperature distribution is not good without a bagwall, one can be put in for the next firing.

A more drastic modification to get more flame and ash effected areas would be to elongate the throat arch area so as to take more pots. One can also stoke wood directly into the chamber, perhaps between rows of shelves, to increase ash effect; however, in my experience, the results of doing this are less satisfying than the results from near the firebox. Whatever you decide you will still be able to devote the bulk of the kiln to glazed wares, fire a normal (not prolonged) wood firing, and get a proportion of ash and flame-marked pots. Not all Bizen-style effects can be achieved with this sort of firing. Also it should be noted that not all stoneware glazes are compatible with effects from ash and flame. You should try all your standard glazes to see how they respond. Glazes that do not respond well to ash and flame can be fired inside other pots, inside saggers, or in zones in the chamber remote from the wood.

A BIZEN KILN

In the Bizen area, kilns are typically fired for between seven and fourteen days, using enormous quantities of wood to maximise the fire-mark effects on the pots. No glaze at all is applied to the pots, though pure ash is sometimes sieved

DIAGRAM 25.3: YU FUJIWARA'S KILN — BIZEN



onto plates etc. that are stacked in parts of the kiln that do not receive much effect. They use both climbing (multichamber) kilns and ana-gama style kilns, and usually the 'firebox' is just the front section of the chamber (first chamber, if it is a multichambered kiln) so that ash and flame effects have direct access to the pots.

As well as the wood stoked into the front of the chamber, wood is often side stoked directly onto some of the pots, and also charcoal is sometimes heaped onto pots in some areas during the firing to make them more interesting.

Much of the upper volume of the chamber is left empty, presumably to enable ash to penetrate to the rear of the chamber. An examination of Diagram 25.3 will show this.

Although kiln shelves are often used nowadays, traditionally the pots were stacked on top of one another, separated by pads of clay and/or rice straw. Sometimes extra pads or 'masks' are put here and there because wherever the pots touch or are touched by a pad or mask, marks and bare patches are left that become part of the decoration. If the mask is loosely draped, graduated effects are possible by vapours penetrating between pot and mask. If it is tightly in contact with the pot, it gives a crisp edge to the mark. In the latter case, rice straw is often placed between the pot and the pad (or mask) to give, *hidasuki* (fire-cord) markings in the bare patch.

The 'hidasuki' effect is possible anywhere where the rice straw is held in place on the pot (e.g. by a pad of clay) or where it is protected from falling off or being blown off by the 'wind' in the kiln. Any exposed rice straw will usually drop off or be blown away and leave no mark. Flat plates separated by rice straw are ideal for hidasuki markings. If the effect is wanted all round a globular or cylindrical pot, it may be wrapped in rice straw and placed inside another pot. The hidasuki effect is best in oxidised areas of the kiln. Quite passable hidasuki pots are produced by firing the pots wrapped in rice straw in an electric kiln.

In areas such as the vent holes between chambers or the flu passages to the chimney, the flame passage is restricted, and the flame moves fast in those areas, depositing little ash but often giving excellent flame markings. In Fujiwara's kiln (See Diagram 25.3) the vent holes were quite large and were packed with pots, and apparently the 'secret chamber' was designed to allow more pots to be subjected to these conditions.

A FEW HINTS

I would like to offer as much encouragement as possible to those potters who would like to explore the possibilities of flame and ash markings from wood firings. For anyone wishing to extend the effects without extending the firing time, here are a few comments:

a. A word of caution for anyone expecting easy success from sieving ash onto the pots as mentioned in relation to some Bizen pots; the results are rather bland by comparison with pots fired close to the fire. There are two main reasons for this. Firstly, genuine fire-marks are the result of a combination of both ash and vapour, not ash alone. The vapour is probably mostly soda from the burning wood. Secondly, the patterns are achieved by white-hot ash and vapour blowing over, under and around the pots at stoneware temperature in the kiln. A whole range of shades, colours and patterns result from the pattern of the flame itself, and these cannot be reproduced by merely sifting ash onto a pot at room temperature.

b. In the King/Harrison style kiln shown in Diagram 25.2, a greater proportion of ash can be taken into the kiln if time is spent agitating the embers in the firebox with a long iron bar introduced through the secondary air vent. As the embers are stirred, one can see the ash fly and stick to the pots in the front of the chamber. Perhaps an extension of this would be to blow in extra ash, and possibly a little salt too, through the same secondary air hole. I have not tried this, but it should increase the ash and vapour effect without prolonging the firing. I recommend a light hand with the salt unless you want it to look like a salt glazing.

c. Some potters put in small pots containing salt in areas perhaps remote from flame effects to get some vapour effect on the clay.

d. If you want to get 'hidasuki' effect, and do not have a rice paddy next door, try any type of grass or straw, or even leaves or twigs. Some work, and some do not. The thing about rice straw, and most grasses in fact, is that they are high in silica, and do not melt; they leave a mark without fusing the pots together. Work done by some Australian Flying Arts

School students in Mackay, however, suggests that vegetation grown near the sea is not suitable as the ash melts (grasses included) at stoneware temperatures. This may be due to a high salt content. Some potters soak their straw or whatever in salt water to get more definite markings, but the results are usually not very nice in stoneware.

EXTENDED FIRINGS — GLAZED AND UNGLAZED POTS

A point worth considering is that certain applied glazes benefit from extended, slowly matured firing. While in Japan, I saw a potter in the Bizen area making excellent Shino ware in his Bizen kiln, and also in the Mino area, I saw a Shino potter experimenting with Bizen-style pots. The two very different styles were compatible because they required the same sort of extended firing, and their kiln-space requirements were complementary; the Bizen style needs lots of ash and flame while the Shino style needs protection from this, and is often fired in saggars in areas unsuitable for good Bizen style pots.

This combination of Bizen style pots and Shino glazed pots has been tried in recent years in Australia with some success (See Ref. No.2) but there is a whole field of research here for someone wishing to work with extended firings to combine applied glazes with flame and ash effects. You will remember that slow maturing was recommended for both celadon and Kuan glazes — perhaps they could be fired inside saggars, or inside other pots, or in areas of the kiln that do not receive much fire effect.

ASH TYPES AND CLAY TYPES

The last point that must be made is that ash types vary greatly, and different firewoods will give different effects. (See the analyses following.)

But even more important than this is the clay or slip that the ash and flame are impinging upon. I have not done enough work on this to comment very intelligently, but I think some of the important variables are as follows: whether the clay or slip is...

1. high in silica or high in alumina
2. vitreous or refractory
3. iron-bearing or iron free
4. high or low in titanium

Note: It would be advisable to avoid highly siliceous clays in extended stoneware firings because of the likelihood of cristobalite cracking.

In the Table following, you will find a list of analyses taken from Reference No.3. It will give a rough guide as to what to expect from the species listed; variations within any one species are great, however, and within one tree, large variations occur between bark, sapwood and heartwood. Unless you have the ability to carry out your own analyses, using wood ash in your glazes is always going to be a matter of try-it-and-see. The reason I have put the sections on ash glaze and rock glaze at the end of this course is that after the systematic work already done, especially in Part I, you will have a much better understanding of glaze principles, of cause and effect. You should be able, therefore, to use ash or rock in a glaze, and when you see the results have some idea what that ash or rock contain and how to adjust the glaze to achieve a desirable effect.

Using natural materials is an exciting way to make glazes: you are never quite sure what is going to happen the first time you try a new material; and you can easily achieve results that are most unlikely to occur if you maintain the analytical approach using pure materials as was done in Part I. I mentioned at the time that this approach was necessary to come to grips with important variables without being confused by impurities etc. And although some excellent glazes are achieved this way, it is a limited approach, limited by our imagination and understanding. You should now be well prepared for that leap into the unknown that occurs when you throw in a handful of ash or rock powder that you have gathered yourself with no reassuring labels or analysis sheet to guide you.

REFERENCES

1. *Layed Back Wood Firing* by King and Harrison.*
2. 'Shino — a Return to a Traditional Approach' by Bill Samuel from *Pottery in Australia. Vol. 21 No. 1.*
3. *Inorganic Constituents in Wood and Bark of New South Wales Forest Tree Species,* Research Note No.45 by Marcia J. Lambert (Forestry Commission of NSW).

*Available from Pottery in Australia, 48 Burton Street, Darlinghurst, Sydney 2010, N.S.W., Australia.

Table 25.1 : WOOD ASH ANALYSES

Extract taken from: *Inorganic Constituents in Wood and Bark of New South Wales Forest Tree Species* by Marcia J. Lambert (Forestry Commission of N.S.W. by permission.

Nutrient content of heartwood from various species, expressed as percentages of the pure ash — reproduced from Annual Report, Director of Forests, Queensland (1918).

Species	Spec. gravity air-dry	Percent of wood		Percentage of pure ash										
		Crude ash	Pure ash	P_2O_5	Al_2O_3	CaO	MgO	K_2O	Na_2O	MnO	Fe_2O_3	SO_3	Cl	SiO_2
Amoora nitidula	.86	1.452	.942	3.14	.01	46.04	9.32	31.68	3.48	.76	.30	2.96	.70	1.62
Angophora spp.	.90				6.70	62.88		9.33						
Auracaria cunninghamii	.56	1.071	.685	1.05	1.19	48.69	10.38	17.89	10.45	.06	1.03	2.13	1.24	5.91
Casuarina torulosa	.93	.681	.437	1.65		64.64	10.28	11.90	4.24	.90	.36	3.58	1.59	1.18
Cedrela australis	.53	1.102	.840	9.39	1.05	59.21	14.37	19.73	6.61	.20	.73	1.31	.72	6.69
Cinnamomum camphora		1.300	1.011	6.35	1.58	23.04	19.49	36.31	5.04		1.65	1.88	.19	4.47
Dissiliaria baloghioides	1.04	1.035	.708	2.62	.38	52.56	7.95	23.36	4.68	.83	.29	1.01	.20	6.13
Eucalyptus acmenioides	1.02	.065	.060	2.08	3.81	9.49	4.38	9.49	10.98	.34	4.53	3.17	.23	51.51
Eucalyptus corymbosa	.99	.089	.075	1.98	1.73	12.50	6.96	12.74	14.64	.42	4.18	3.49	.68	40.66
Eucalyptus corymbosa	.99	.164	.115	.84	.17	13.05	18.01	25.93	11.68	.09	3.66	1.67	.71	24.19
Eucalyptus microcorys	1.01	.131	.103	.97	2.16	26.98	34.16	3.95	3.31	.38	1.55	3.34	.18	23.06
Eucalyptus microcorys	1.02	.251	.183	.40	1.09	52.15	25.58	2.41	6.84	.18		1.93	.58	8.96
Eucalyptus pilularis	.88	.119	.098	2.74	2.06	14.36	11.05	15.92	18.73	.79	3.11	3.51	.69	27.05
Eucalyptus propinqua	1.06	.180	.162	6.51	2.96	28.88	7.74	11.39	9.08	.79	2.31	4.12	.87	25.36
Eucalyptus resinifera	.98	.054	.047	.76	1.61	17.30	4.81	9.16	14.41	.25	4.79	6.24	.49	40.18
Eucalyptus siderophloia	1.12	.085	.078	3.87	3.33	22.80	8.39	6.44	12.19	1.38	2.78	5.75	.47	32.60
Eucalyptus tereticornis	1.01	.140	.131	14.04	3.34	19.18	3.62	9.14	11.68	1.21	2.74	3.77	.46	30.85
Eucalyptus tesselaris	1.01			15.65		55.75		8.61						
Euroschinus falcatus	.48	.926	.629	2.92	.29	37.76	18.82	33.88	1.65	.90	.25	1.09	.94	1.50
Flindersia oxleyana	.74	.446	.325	2.25	.27	45.23	17.14	14.47	3.02	2.45	.47	10.16	.44	3.51
Flindersia schottiana	.64	.781	.517	2.25	.12	51.88	15.77	20.54	2.40	1.68	.20	1.56	.21	3.40
Myrtus hillii	.89	2.043	1.125	1.85		64.42	24.37	6.65	1.02	.07	.20	.93	.07	.44
Naba fasciculosa	.89	2.792	1.859	1.77	.72	62.78	21.78	8.32	1.40	.87	.39	1.50	.06	.42
Polyalthia nitidissima	.90	.768	.678	12.23	.28	28.31	28.31	13.10	8.31	2.81	.43	2.62	.24	2.65
Sideroxylon pohlmanianum	.93	.822	.589	3.43		45.84	22.16	19.87	.86	.91	.68	4.24	.49	1.51
Syncarpia laurifolia	1.00	.367	.367	.35	1.26	1.88	1.83	1.20	4.08	.08		.82		89.74
Tarrietia argyrodendron	.96	1.494	.921	2.72		52.62	22.25	15.50	1.33	.73	.23	3.29	.03	1.62
Tristania conferta	.86	.970	.830	.34	.65	31.13	9.10	7.90	6.83	.46		.70	5.15	38.90
Vitex ligmun-vitae	.89	1.135	.706	4.15	.02	54.71	9.56	26.26	2.57	.14	.19	1.29	.06	1.06
Weinmannia lachnocarpa	.94	1.444	.902	2.70	.14	51.45	27.21	9.96	1.25	1.02	.21	4.96	.06	1.02

26 ROCK GLAZES

The subject of geology for potters is very well covered by Cardew in his *Pioneer Pottery*, and rather than repeat that here, I merely refer you to his text. I will, however, expand a little on his treatment of the chemical classification and composition of igneous rocks. Igneous rocks are those that at some stage have been partially or completely molten. Their composition is such that most will melt at stoneware temperatures to give a glaze. Hence, they are of special interest to potters.

IGNEOUS ROCKS

Igneous rocks may be classified in many ways, but the most useful to us is the chemical classification where the starting point is the percentage of silica. Under this system the rocks may be regarded as 'acid' (66% SiO_2 or more), 'intermediate' (between 66% and 52% SiO_2) and 'basic' (less than 52% SiO_2). The typical acid rock would be granite, and the typical basic rock would be basalt.

Table 26.1 taken from Cardew (originally from *Teach Yourself Geology* by A. Raistrick (English University Press, 1950)) shows the acid-basic classification from left to right. There are three parallel series: volcanic, hypabyssal and intrusive. The intrusive rocks are formed by an enormous body of molten material pushed up near the surface but remaining still beneath the surface as it cools slowly. The size of the crystals of individual minerals is relatively large. Most intrusive rocks are acid, typically granite. Volcanic rocks are cooled quickly, having been ejected onto the surface of the earth as lava flows etc. and therefore have a much smaller crystal size. Most volcanic rocks are basic, typically basalt. The hypabyssal rocks form an intermediate group between the other two.

The reason this classification is so useful to us is that as rocks decrease in silica, from acid to basic, there is a distinct trend in most other important oxides, in particular, K_2O, Na_2O, CaO, MgO, FeO, TiO_2.

Alumina is reasonably constant over the range, or at least it shows no trend to increase or decrease as one moves from acid to basic rocks. K_2O seems typical of the more acid rocks, Na_2O and CaO of the intermediate to basic range. MgO and FeO are typical of basic rocks but are also plentiful in the intermediate range. There

TABLE 26.1: IGNEOUS ROCKS CHEMICAL CLASSIFICATION

	ACID	INTERMEDIATE		BASIC
	Light Colour Low Specific Gravity (eg 2.65)	Alkali Series	Calc-Alkali Series	Dark Colour, High Specific Gravity (eg 3.3)
Volcanic	Rhyolite (Pumice)	Trachyte	Andesite	Basalt
Hypabyssal	Quartz-Felsite	Micro-Syenite	Micro-Diorite	Dolerite (Syn. Diabase)
Intrusive	Granite	Syenite	Diorite	Gabbro

is also a significant presence of TiO_2 in many basic rocks, averaging around 1.5-2%, which will have a noticeable effect if a high percentage of the rock is used in a glaze. Broadly speaking, the result of these trends is that acid rocks tend to give pale glazes, while basic rocks usually give high iron glazes, such as teadust (because of the MgO), tenmoku, rust, and other dark glazes.

See Table 26.2 for analyses of a range of igneous rocks. The analyses I have

TABLE: 26.2 IGNEOUS ROCKS - 'TYPICAL' ANALYSES

(Note: Page and number references to B.M.R. Bulletin No. 65, Reference No. 3.)

VOLCANIC SERIES:

	ACID		INTERMEDIATE				BASIC	
	P. 116 No. 2 Rhyolite		P. 164 No. 4 Trachyte		P. 148 No. 24 Andesite		P. 218 No. 87 Basalt	
	Ox. Wt	SEGER	Ox. Wt	SEGER	Ox. Wt	SEGER	Ox. Wt	SEGER
SiO_2	74.28	9.8	65.31	5.5	54.25	3.8	46.29	1.7
Al_2O_3	11.27	.88	12.08	.60	19.46	.81	13.71	.29
Fe_2O_3	1.93	.1	5.12	.16	3.16	.08	3.03	.04
FeO	0.58	.06	3.07	.22	4.27	.25	9.14	.28
MgO	0.44	.09	0.96	.12	2.75	.29	9.50	.51
CaO	1.15	.16	2.50	.23	5.81	.44	8.60	.33
Na_2O	2.74	.35	4.91	.40	3.56	.24	3.26	.11
K_2O	4.77	.40	4.72	.25	0.62	.03	1.62	.04
TiO_2	0.25	.02	0.49	.03	1.82	.10	2.95	.08
Mol. Wt		772		502		406		214

INTRUSIVE SERIES:

	ACID		INTERMEDIATE				BASIC	
	P. 38 No. 37 Granite		P. 74 No. 6 Albitite		P. 83 No. 8 Diorite		P. 93 No. 3 Gabbro	
	Ox. Wt	SEGER	Ox. Wt	SEGER	Ox. Wt	SEGER	Ox. Wt	SEGER
SiO_2	71.82	8.1	66.13	5.5	61.09	3.3	46.3	1.9
Al_2O_3	14.09	.94	19.92	.98	15.75	.50	14.44	.35
Fe_2O_3	0.75	.03	0.60	.02	2.94	.06	9.08	.12
FeO	1.32	.12	0.19	.01	1.77	.08	7.2	.25
MgO	0.45	.08	0.12	.01	4.55	.36	7.9	.49
CaO	1.38	.17	0.57	.05	6.43	.37	11.5	.51
Na_2O	2.57	.28	10.83	.88	4.69	.24	Trace	—
K_2O	6.61	.48	1.02	.05	0.73	.02	Trace	—
TiO_2	0.91	.08	0.31	.02	0.87	.04	0.24	.01
Mol. Wt		678		502		318		238

chosen seem fairly typical of their respective classes although, for example, other granites will vary considerably from the 'typical' granite analysis I've chosen. I have given a volcanic series and an intrusive series. These analyses are chosen from several thousand listed in Bulletin No.65, *Chemical Analyses of Australian Rocks. Part I: Igneous and Metamorphic* by G.A. Joplin (available from: Publication Sales, Bureau of Mineral Resources, PO Box 378, Canberra City, ACT 2601).

IDENTIFYING ROCKS AND MINERALS

It takes years of study to recognise rocks and minerals in the field with any degree of proficiency. This ability is very useful, of course, but not really essential to us. Much of Australia has been covered by geological surveys, and much of this information is available to us if we know where to look and ask. I think that for a potter who knows little of geology, the best approach is either to get a geologist to help you identify rocks (or a gem/rock/mineral enthusiast) or obtain the appropriate geological map/s for your area and do a few field trips. If you are at all interested in using local materials for clays or glazes, you should find out what information is available for your area from the Department of Mines. For example, if you write to: Department of Mines, 41 George Street, Brisbane, you could obtain copies of the following:

1. The appropriate geological map/s for your area in the 'Australia 1:250,000 Geological Series'. If your map is currently out of print, you could request a photostat copy which they will do for a small fee. The photostat is harder to read because of the lack of colour, but it is almost as good.
2. The 'Geological Survey of Queensland List of Publications and Reports', and the price list. Many areas, especially mining areas, have had detailed geological surveys and reports done, and if you go through this list, you will find if there is anything relevant to your area.
3. In the list mentioned above, you will find: 'Geological Survey of Queensland Report No.20 — Resources of Ceramic Clay Materials in Queensland'. It lists the known useful clay deposits in Queensland, dealing mainly with larger deposits, but some smaller deposits that have been reported to the Department of Mines are listed. The report contains geological sketch maps for several areas: Beaudesert, Warwick, Dinmore, South Burnett, Maryborough, Rockhampton, Mackay.

I find geological maps extremely useful — as well as showing what rocks are where, they show mines and quarries, and recorded deposits of clay, limestone, dolomite, diatomaceous earth, cobalt, manganese, copper etc. You will often, however, need local help to locate on the ground something that is recorded on the map.

If you are seeking local ores to use as ceramic colourants (cobalt, manganese, copper ores etc.) the following technique may be useful in identifying them and assessing their usefulness as colourants. It is a crude version of the 'Borax Bead Test', which is described in textbooks on mineralogy, such as *A Textbook of Mineralogy* by Dana and Ford. The idea is that pure borax when melted forms a glass, and any ceramic colourant that is added will give a characteristic colour response. The technique I use is to crush a little of the ore to powder with a clean hammer, mix a little of the fine powder with some borax, put the mixture on a piece of white refractory fired clay (e.g. white firebrick) and melt it with an oxy torch or an L.P. gas torch. You will probably be able to recognise the colour responses by now. Using this technique with known ores, I have obtained blue with cobalt, violet with manganese, green and red with copper, and honey with iron. This is rather crude compared with the proper borax bead test but if, for example, you got to an area that is supposed to have, say, cobalt ore, you can identify the ore very quickly in the field with a gas torch and some borax.
(*Note:* The borax will be melted in oxidation or reduction, depending on which part of the flame you use. The oxidation zone is just beyond the visible tip of a clean flame. **Take suitable precautions against the possibility of the piece of refractory clay spitting or exploding.)**

CRUSHING AND GRINDING THE ROCK

Sources of pulverised rock and ways of pulverising your own were discussed in Chapter 4.

IVAN ENGLUND ON ROCK GLAZES

Ivan Englund has used rock glazes extensively for many years, and his approach is very simple, direct, and relevant to the kind of situation that applies to many Australian potters in isolated places without sophisticated equipment or analyses of local materials. It is true that he usually works out his glaze recipes using actual or assumed analyses to produce a glaze of a desired molecular formula, but he also uses empirical means and rules of thumb that provide a good guide when analyses are not available. He has written several articles in the *Pottery in Australia* magazine and a booklet (see References). I am very grateful to him for making time for me to obtain much of the information that follows.*

*(*Note:* You will find his approach set out in more detail in his recently published book, *Rock Glazes.* See Ref. No.8.)

In the past, using the molecular (Seger) formula approach, Ivan would calculate a recipe to include as much rock as possible while giving alumina/silica values of around 0.33 Al_2O_3, 3.3 SiO_2. The general formula for his stoneware glazes was: RO, 0.33 Al_2O_3, 3.3SiO_2. He has now amplified this approach to cover a wide range of alumina/silica values, in much the same was as was done in the biaxial blends for the base glaze exercises earlier in this course.

He says that virtually the full range of igneous rocks, from granite to basalt, will give glazes at stoneware temperatures; granites may need a little extra flux (he normally uses whiting), and basalts may benefit from adding silica. He gives the following starting-point recipes that should approximate very roughly to the .33 Al_2O_3, 3.3SiO_2 figures:

Granite Glaze	Basalt Glaze
92%Granite	70% Basalt
8% Whiting	20% Silica
	10% Whiting

(To suspend these glazes, 5% ball clay or 2% Bentonite could be added without substantially changing the melting point or the nature of the glaze.)

Almost all of Ivan's personal glazes are, however, for raw glazing, and he calculates about 11% of WA bentonite into the recipe.

(*Note:* Western Australian bentonite is low in alumina and high in MgO).

He does not add feldspar to his glazes as a flux since this would in most cases increase alumina to more than he desires; however, he agrees that one could still maximise rock content and add a little feldspar as a flux.

Ivan does not have any rock crushing or milling equipment. He uses only rock dusts that are readily available from rock crushing plants (producing blue-metal etc.) or decomposing rocks that are easily crushed. He says that quite often a decomposing rock gives virtually the same result as solid rock mined from the same deposit; and if they are different, the solid rock will not necessarily be more interesting in a glaze than the decomposed and more easily crushed version.

The glazes are usually sieved through a 60-mesh sieve though the granite glazes, with hard-to-melt free silica, may be put through a 100-mesh. He says he should get a ball mill, but adds that he is not a fine-ness fanatic. I would add that a ball mill will make a difference to many or most rock glazes, but whether you prefer the result is another matter. If you would rather have a refined result, then try a ball mill. See Chapter 4 for information on them.

In his article 'Basalt Glazes' in *Pottery in Australia,* Vol.17, No.2 (page 12), Ivan Englund shows how he uses an average analysis for basalt (if an accurate analysis is not otherwise available) which he calls 'Avbas'. He gives a Seger formula for his average basalt as:

0.042 K_2O
0.131 Na_2O 0.405 Al_2O_3 2.152 SiO_2
0.420 CaO 0.206 (M.P.) Fe_2O_3
0.407 MgO Mol. Wt: 255

(*Note:* The figure of 0.405 M.P. of Alumina has been corrected from what was quoted in the original article — similarly the Mol. Wt.)

Ivan also offers the following 'Avgran' formula, which is an average of many Australian granites:

0.24 K_2O
0.29 Na_2O 0.82 Al_2O_3 7.00 SiO_2
0.29 CaO 0.12 Fe_2O_3
0.18 MgO Mol. Wt: 590

See also the 'typical' values I use in this unit (Tables 26.2 & 26.3).

To get more accurate analyses of your local rocks, you could try the following:

1. Local offices dealing with mining or geology.
2. Local universities or technical colleges.
3. Department of Mines in Brisbane.
4. Published analyses, e.g. *Bureau of Mineral Resources Bulletin No.65,* mentioned previously.

SOME SIMPLE TESTING PROCEDURES

Here are some simple tests that are good for investigating the usefulness of any material as a sole or a major glaze ingredient; so these tests can be used not only for igneous rocks, but also for things like frits, wood ashes etc., anything that will give, or almost give, a glaze by itself. Here the tests are written out for use with igneous rock glazes, but you could modify the techniques to examine other materials.

1. Spot Tests

It is only about ten minutes work to crush and grind a small sample of almost any rock, enough to apply to two or three assessment tiles. Collect and label small samples of likely looking rocks to test for usefulness as glazes. Using a clean hammer, and a clean heavy piece of steel ('clean' to avoid contamination by rust), pulverise a small piece of the rock until it is very fine sand, then put it in a mortar, add a little water, and grind it with the mortar and pestle until it no longer feels gritty. About a teaspoonful is adequate. Put a thick dob of the ground rock paste onto several assessment tiles. Repeat with other rock samples, and also samples of crusher dust etc., putting samples onto the same tiles. Place the assessment tiles in hot spots, cold spots etc., and fire. In particular, place one tile in the hottest spot in the kiln. If you use a gas kiln, place one tile in front of a burner. Usually you learn more by overfiring than by underfiring.

2. Line Blends

These are what I call 'Quick Casual Line Blends', using the mortar and pestle line blending technique as outlined in Chapter 15. It is just a quick way of adding in progressive amounts of a second ingredient. For example, if using granite, try adding some whiting, (as Ivan Englund suggests) or some wood ash; if using basalt, try silica or clay or feldspar or wood ash. The idea is not to bother weighing anything — just start with, say, a dessertspoonful of the rock dust, then add the second ingredient to the mortar in progressive equal steps to give, say, 5% (approximately by volume), 10%, 15%, 20% etc. Sample after each addition and put the samples onto assessment tiles. You can cover a lot of ground this way with little effort; and if anything worthwile appears, do more accurate experiments to pin it down.

3. Biaxial Blends

To get some idea of the effect of varying alumina and silica with the rock as a major ingredient, we can do a Quick Casual Biaxial Blend. It gives a grid of nine glazes covering a range of alumina and silica values as we have done before, but you will not know the actual figures in molecular parts unless you have rock analyses and go to the trouble to work them out.

See Diagrams 26.1 and 26.2 for the general layout of the grid, and Tables 26.4 and 26.5 for some suggested recipes for the corner glazes.

I have worked out a set of corner glazes for acid rocks, and one for basic rocks. I have used the analyses for granite and basalt in Table No.26.2, and worked out molecular formulae for a 'typical' granite and 'typical' basalt. See Table 26.3.

TABLE 26.3

	GRANITE			BASALT		
	%	Molecular Parts		%	Molecular Parts	
SiO_2	71.82	8.11		46.29	1.68	
Al_2O_3	14.09	0.94		13.71	0.29	
Fe_2O_3	0.75	0.03		3.03	0.04	
FeO	1.32	0.12		9.14	0.28	
MgO	0.45	0.08		9.50	0.51	
CaO	1.38	0.17	RO=1.0	8.60	0.33	RO=1.0
Na_2O	2.57	0.28		3.26	0.11	
K_2O	6.61	0.48		1.62	0.04	
TiO_2	0.91	0.08		2.95	0.08	
		Mol. Wt: 678			Mol. Wt: 214	

Using these formulae, I have worked out the corner glazes for two biaxial blends, one for granite, one for basalt, to be used for acid and basic rocks respectively. See Tables 26.4 and 26.5. (Note the addition of whiting to both sets. You will find, however, that many basic rocks need no added CaO to make good glazes.

TABLE 26.4 ACID ROCKS

Material	A	B	C	D
Granite	77	60	90	70
Kaolin	15	10	—	—
Whiting	8	5	10	7
Silica	—	25	—	23

TABLE 26.5 BASIC ROCKS

Material	A	B	C	D
Basalt	65	33	90	50
Kaolin	28	18	—	—
Whiting	7	4	10	6
Silica	—	45	—	44

TABLE 26.6

Material	A	B	C	D
Basalt	75	40	100	50
Kaolin	25	20	—	—
Silica	—	40	—	50

Table 26.6 shows corner glazes that cover much the same area as in Diagram 26.2, but with the whiting eliminated. The Table will also work for most wood ashes, substituting wood ash for basalt. I actually prefer this Table to the previous two as a starting point because of the absence of additional fluxes other than what comes from the rock or ash. One of the main reasons these days for using natural materials is for the individual qualities they give resulting from their unique set of fluxes and colouring oxides. It makes sense therefore to leave this part alone in preliminary experiments, and vary just the alumina and silica to more clearly see what special things the material under study has to offer.)

So if you know you have an acid rock, use Table 26.4, and for a basic rock, use Table 26.5 (or Table 26.6). Even though the true analysis of your rock will probably vary considerably from the analyses in Table 26.3, nevertheless, if you use the appropriate table, you will get a good spread of alumina/silica variation; and most of the glazes should melt at stoneware temperatures. If the rock is an intermediate rock, such as trachyte or diorite, you could have a stab at an intermediate set of corner glazes by taking values between Table 26.4 and Table 26.5. For example, for Glaze A, take the percentage or rock dust somewhere between 77% and 65%; for kaolin, it would be somewhere between 15% and 28% etc.

To give you some idea what these experiments look like in theory, I have indicated the areas they cover on Diagrams 26.1 and 26.2 using the analyses for granite and basalt listed above. Naturally, the real areas covered vary depending on the composition of the actual rock used.

DIAGRAM 26.1 - FOR ACID ROCKS

RO for Granite Series approx:
0.28 K_2O
0.17 Na_2O
0.51 CaO
0.04 MgO

To get lower alumina and silica values in the Granite Series, you would have to increase fluxes (e.g. CaO, BaO, ZnO, MgO, Li_2O) and reduce the rock dust.

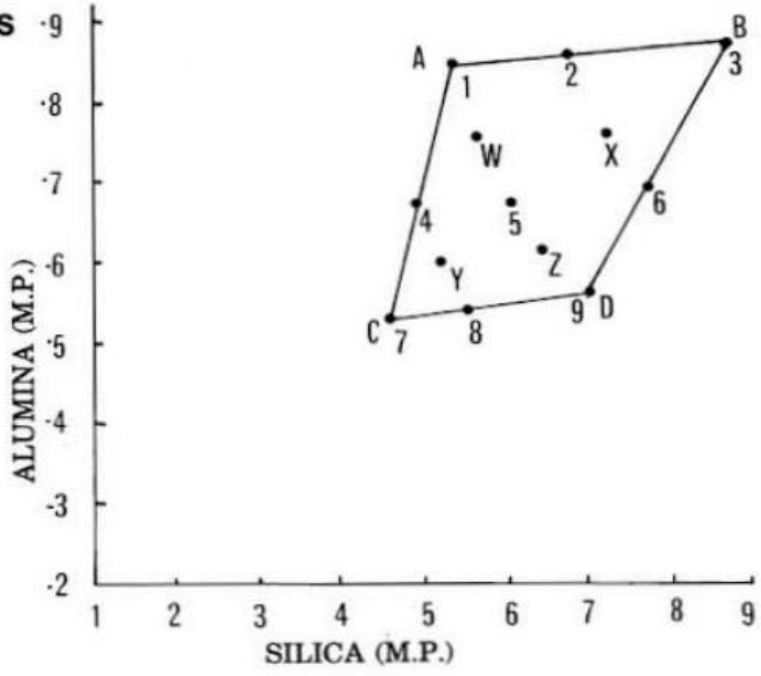
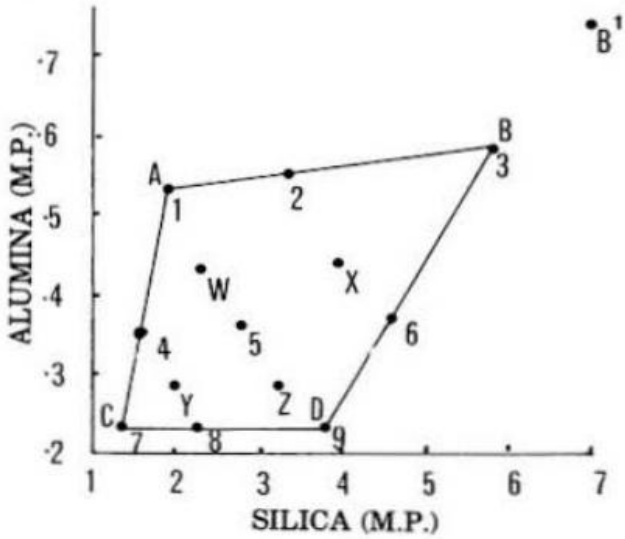


DIAGRAM 26.2 — FOR BASIC ROCKS

RO for Basalt Series approx:
0.04 K_2O
0.10 Na_2O
0.46 CaO
0.40 MgO

If you want to examine glazes with higher alumina and silica than presently used in the Basalt Series, you can simply use more kaolin and silica in Glaze B. For example, if Glaze B is changed to: 28% Basalt, 21% Kaolin; 3.4% Whiting and 47% Silica, then B on Diagram 26.2 will be at 0.73 Al_2O_3 and 7.12 SiO_2 (marked 'B^1').



Quick Casual Biaxial Blend (Varying Alumina and Silica)
Procedure:
Weigh out the four corner glazes.

Make them all up to the same volume with water as for normal volumetric blending (any convenient volume). (Volumetric blending described in Chapter 6.)

Sieve them if necessary, but there should not be any significant volume of solids left on the sieve: this would indicate the rock needs finer grinding for the chosen sieve size.

Using any convenient measure, take *equal* volumes of:

A and B to give Glaze No.2
A and C to give Glaze No.4
B and D to give Glaze No.6
C and D to give Glaze No.8
A, B, C and D to give Glaze No.5

These glazes,along with the four corner glazes, give you the nine glazes for the grid.

Remember to keep the corner glazes well agitated while sampling, to prevent settling out.

Note: It would be easy to obtain ('quickly and casually') four more glazes that fill out the ground even more, if you have remnants of glazes 2, 4, 6 and 8, immediately after the initial blending and sampling: (See Diagrams 26.1 & 26.2).
Equal amounts of:

2 and 4 give Glaze W
2 and 6 give Glaze X
4 and 8 give Glaze Y
6 and 8 give Glaze Z

Alternatively, you can make them up from the original Corner Glazes -- A, B, C and D:

W:	9A	3B
	3C	1D

X:	3A	9B
	1C	3D

Y:	3A	1B
	9C	3D

Z:	1A	3B
	3C	9D

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BORAX BEAD TEST

4. TREATMENT OF THE PLATINUM WIRE

515 Use of the Fluxes – The three common fluxes are borax, salt of phosphorus, and carbonate of soda (p.361). They are generally used with the platinum wire, less often on charcoal (see above). If the wire is employed it must have a small round loop at the end; this is heated to redness and dipped into the powdered flux, and the adhering particles fused to a bead; this operation is repeated until the loop is filled. Sometimes in the use of soda the wire may at first be moistened a little to cause it to adhere.

When the bead is ready, it is, while hot, brought in contact with the powdered mineral, some of which will adhere to it, and then the heating process may be continued. Very little of the mineral is in general required, and the experiment should be commenced with a minute quantity and more added if necessary. The bead must be heated successively first in the oxidizing flame (O.F.) and then in the reducing flame (R.F.), and in each case the colour noted when **hot** and when **cold**. The phenomena connected with fusion, if it takes place, must also be observed.

Minerals containing sulphur or arsenic, or both, must be first **roasted** (see p.365) til these substances have been volatilised. If too much of the mineral has been added and the bead is hence too opaque to show the colour, it may, while hot, be flattened out with the hammer, or drawn out into a wire, or part of it may be removed and the remainder diluted with more of the flux.

With salt of phosphorous, the wire should be held above the flame so that the escaping gases may support the bead; this is continued till quite fusion is attained.

It is to be noted that the colours vary much with the amount of material present; they are also modified by the presence of other metals.

516 Borax – The following list enumerates the different coloured beads obtained with borax, both in the oxidizing (O.F.) and reducing flames (R.F.), and also the metals to the presence of whose oxides the colours are due. Compare further the reactions given in the list of elements (Art.518).

Colour in Borax Bead	Substance
	1. OXIDIZING FLAME
Colourless, or opaque white	Silica, calcium, aluminum; also silver, zinc, etc. Iron, cold – (pale yellow, hot, if in small amount).
Red, red-brown to brown	Chromium (CrO_3), hot – (yellowish green, cold).
	Manganese (Mn_2O_3), amethystine-red – (violet, hot).
	Iron (Fe_2O_3), hot – (yellow, cold) – if saturated.
	Nickel (NiO) red-brown to brown, cold – (violet, hot).
	Uranium (UO_3), hot – (yellow, cold).
Green	Copper (CuO), hot – (blue, cold, or bluish green if highly saturated).
	Chromium (CrO_3), yellowish green, cold – (red, hot).
Yellow	Iron (Fe_2O_3), hot – (pale yellow to colourless, cold) – but red-brown and yellow if saturated.
	Uranium (UO_3), hot, if in small amount; paler on cooling.
	Chromium (CrO_3), hot and in small amount – (yellowish green, cold).
Blue	Cobalt (CoO), hot and cold.
	Copper (CuO), cold if highly saturated – (green, hot).
Violet	Nickel (NiO), hot – (red-brown, cold).
	Manganese (Mn_2O_3), hot – (amethystine-red, cold).

2. REDUCING FLAME (R.F.)

Colourless	Manganese (MnO), or a faint rose colour.
Red	Copper (Cu_2O, with Cu), opaque red.
Green	Iron (FeO), bottle-green.
	Chromium (Cr_2O_3), emerald-green.
	Uranium (U_2O_3), yellowish green if saturated.
Blue	Cobalt (CoO), hot and cold.
Gray, turbid	Nickel (Ni).

INDEX

A
A.F.A.S., ix
alkali fluxes, 5, 44
alumina, 36
alumina matts, 139
alumina/silica ratio, 41
alumina, sources of, 40
anagama, 184, 194
analysis sheets, 4
anorthite, 13, 92
application of glazes, xiii
ash, analyses, 199
ash glazes, natural, 194
ash, wood, 20, 194
ash, preparation, 20
assessment of results, 35
assessment tiles, 17, 31, 32
assessment tiles, firing of, 31
atoms, 10
'avbas', 203
aventurine glaze, 129
'avgran', 203

B
ball clay Q.A., 101, 103
ball mills, 21
BaO in celadons, 175
BaO in iron glazes, 164
barium carbonate, poisonous nature of, 74
barium glazes, 74
barium matts, 136
barium, sources of, 74
baseline, 25
baseline grid, 25
biaxial blends, 26, 28, 29
Bizen clay, 194
Bizen firing, 196
black Seto ware, 183
blended glaze recipes, calculation of, 116
borax, 44
borax bead test, 202, 207
boric oxide, effect on copper red glazes, 190
Broken Hill feldspar, 103

C
calcining calculations, 110
calcite, 7
calcium matts, 139
CaO in glazes, 43
celadon, 163, 173
celadon, blue, 175, 177
celadon, bubbles in, 178
celadon, effect of base glaze on, 173
celadon, Lung Chuan, 175
cha-no-yu, 183, 194
chrome red glaze, 144
Chun-blue, 49, 53, 71, 145
Chun-blue, factors affecting, 145
Chun-blue in iron glazes, 165
clay-glaze interface, 135
colloidal silica, 146
colourless iron, 164, 170
conversion chart, 92
conversion factor, 165
copper glazes, 188
copper red glazes, 189
copper red glazes, firing of, 191
copper ruby, 189
corner glazes, xii
crazing, 38, 156
cristobalite, 157
crystal growth, 126
crystallisation, process of, 125
crystals, 49, 53, 65, 71, 124

D
data, xiv, 45
devitrification, 124
dolomite, 7, 62, 65
draw trials, 121

E
engobes, 151, 153
eutectic, 84
eutectic composition, 84
eutectic temperature, 84
eutectic trough, 90
experiments, preliminary comments to, 45

F
feldspar, 5, 8
ferric chloride, 186
ferrous silicate, 147
fire colour in Shino glazes, 183, 184, 186
firing, xiii
firings for base glaze sets, 47
flambe glaze, 189, 192
flux-alumina matts, 37
fluxes, diversification of, 91
flux matts, 37, 136
four question technique, 92
frits, alkaline, 5

G
glaze fit, 38, 156
grey Shino, 184
group study, 2

H
Hidasuki markings, 197
honey glaze, see Chapter 20

I
igneous rocks, 200
individual tiles, 17, 33, 34
interface, clay-glaze, 135
intermediate blends, 115
iron chloride, 186
iron, colourless, 164, 170
iron glazes, 158
iron oxide, forms of, 158, 170
iron oxide, solubility of, 164
iron silicate, 177
isotherm, 90

J
Japanese Shino glaze, 183, 186
Japanese tea ceremony, 183

K
Kaki glaze, 61, 158
kaolin, 7, 8
kiln setting clay, 17
kiln wadding, 17
KNaO, 5, 44
Kuan glaze, 57, 140, 179

L
labelling, 24
lime/alkali balance in iron glazes, 164
lime/alkali glazes, 43
lime in glazes, 43
limits, xii
line blend, 20
liquidus line, 84
liquidus plane, 90
lizard skin glaze, 65

M
machine aesthetic, 183
magnesia, effect in copper red glazes, 191
magnesia, role in iron glazes, 164
magnesia, sources of, 62
magnesium carbonate, 7, 62
magnesium glazes, 62
magnesite, 7, 62
marbled Shino glaze, 184
materials, xii
matt glazes, 37, 134
methodology, xii, 120
molecular parts, 15
molecules, 11
M.P., 15

N
nepheline syenite, 5
nepheline syenite Shino, 185, 186
nickel reds and blues, 129, 132
nucleation, 125
numbering system for glazes, 47

O
oatmeal glaze, 65
oilspot tenmoku glaze, 166
Ogama, 184, 185
opacifiers, 141
opaque glazes, 141, 156
orangepeel effect, 37
order of calculation, 92, 108
Oribe ware, 183
oxides, 12
oxide weight charts, 45
oxide weight percentage, 13
oxy probe, 47

P
partial blends, 115
parts chart, 30
parts chart calculations, 111
peach bloom glaze, 190, 192
percentage calculation, 94, 99
percentage method, 107
phase equilibria diagrams, 84
pigments, 153
pigments, recipes of, 154
pigskin effect, 65
pink matt glaze, 35, 37
preparation of glazes, xii
pyroxene crystals, 62, 128, 131, 163, 168

Q
Queensland Potters' Association, ix

R
raw materials, 4
recipe, 13
recipe charts, 45
recording data, 24
red Shino glaze, 184
results, xiii
results charts, 45
RO, 12
rock dust, 21, 204
rust break (in iron glazes), 165
rust glaze, 158, 159, 164

S
salt, 44
salt in Shino glazes, 185, 186, 187
sang-de-boeuf glaze, 189, 192
Seger formula, 13
seeding of crystals (artificial), 128
Shigaraki clay and firing, 194, 195
Shino glaze, 183
shiny glazes, 37
silica, 36
silica, colloidal, 146
silica matt glazes, 53, 65, 139
silicon carbide, 154, 191
simultaneous equations, 104
slips, 150, 151
slips, coloured, 153
slips, recipes of, 152
slips, trouble-shooting of, 152
starting points, 25
striking, 189, 192
stringing, 37, 49, 53
sugary glazes, 38
supercooled liquid, 124
suspender, 181

T
talc, 7, 62
teadust glaze, 158, 159, 162, 163, 164, 165, 168
teadust effect, 168
tenmoku, 158, 165, 170, 171
tenmoku, oilspot, 166
tessha glaze, 61, 158, 169, 170
test firings, 121
tin oxide, effect on copper red glazes, 191
titanite crystals, 128
tomato red glaze, 169
trial and error (calculation) 104
triaxial diagrams, 87, 114
turquoise copper glaze, 188

U
unity formula, 94
unity formula for iron glazes, 158

V
vaporisation of fluxes, 39
vapour imprint diagrams, 39
volumetric blending, biaxial, 28, 29
volumetric blending, line, 21, 23

W
white tenmoku, 183
whiteware, 150
whiting, 7, 15, 43
woodash, 20
woodash analyses, 199

Y
yellow Seto glaze, 177, 183

Z
zinc crystal glazes, 128, 130
zinc glazes, 68
zinc oxide, sources of, 68
zinc oxide, vaporisation of, 39, 71